PB86-232576

National Surface Water Survey: Eastern Lake Survey (Phase 1 - Synoptic Chemistry). Quality Assurance Plan

Lockheed Engineering and Management
Services Co., Inc., Las Vegas, NV

Prepared for

Environmental Monitoring Systems Lab.
Las Vegas, NV

Feb 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-232576

EPA/600/4-86/008
February 1986

NATIONAL SURFACE WATER SURVEY
EASTERN LAKE SURVEY (PHASE I -- SYNOPTIC CHEMISTRY)
QUALITY ASSURANCE PLAN

by

S. K. Drousé, D. C. Hillman, L. W. Creelman, and S. J. Simon
Lockheed Engineering and Management Services Company, Inc.
Las Vegas, Nevada 89114

Contract No. 68-03-3249

Project Officer
Eugene P. Meier
Advanced Monitoring Systems Division
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada 89114

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89114

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/4-86/008	**2.**	**3. RECIPIENT'S ACCESSION NO.** PB86 232576/AS
4. TITLE AND SUBTITLE NATIONAL SURFACE WATER SURVEY EASTERN LAKE SURVEY (PHASE I -- SYNOPTIC CHEMISTRY) QUALITY ASSURANCE PLAN		**5. REPORT DATE** February 1986 **6. PERFORMING ORGANIZATION CODE**
7. AUTHOR(S) S.K. Drouse', D.C. Hillman, L.W. Creelman, and S.J. Simon		**8. PERFORMING ORGANIZATION REPORT NO.**
9. PERFORMING ORGANIZATION NAME AND ADDRESS Lockheed Engineering and Management Services Company 1050 E. Flamingo Road Las Vegas, NV 89109		**10. PROGRAM ELEMENT NO.** CCVNIA **11. CONTRACT/GRANT NO.** 68-03-3249
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring Systems Laboratory - LV, NV Office of Research and Development U.S. Environmental Protection Agency Las Vegas, NV 89114		**13. TYPE OF REPORT AND PERIOD COVERED** Final, NA **14. SPONSORING AGENCY CODE** EPA/600/07

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The National Surface Water Survey (NSWS) of the National Acid Precipitation Assessment Program is a three-phase project to evaluate the current water chemistry of lakes and streams, determine the status of fisheries and other biotic resources, and select regionally representative surface waters for a long-term monitoring program. A synoptic survey of eastern lakes is part of the first phase of the NSWS. This manual delineates the quality assurance plan for the Eastern Lake Survey-Phase I.

This Quality Assurance Plan is based on the guidelines and specifications provided by the Quality Assurance Management Staff (QAMS) of the Office of Research and Development, 1980. The sixteen points required in the guidance are addressed in the plan. In addition, a number of appendices provide data forms used in the survey, questionnaires used for field and laboratory on-site evaluations, the data package completeness checklist and a copy of the batch data verification report.

The methods used by the contract analytical laboratories are listed in this plan and are described in detail in a companion document (EPA 600/4-86/009, Hillman, et al.). The internal quality control used by the contract analytical laboratories is described in detail in this plan. A system of double blind audit samples of both synthetic composition and natural lake waters is described.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	**19. SECURITY CLASS** *(This Report)* Unclassified	**21. NO. OF PAGES** 226
	20. SECURITY CLASS *(This page)* Unclassified	**22. PRICE**

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

The information in this document has been funded wholly or in part by the U.S Environmental Protection Agency (EPA) under contract number 68-03-3249 to Lockheed Engineering and Management Services Company, Inc. (Lockheed-EMSCO). It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

The National Surface Water Survey of the National Acid Precipitation Assessment Program is a three-phase project to evaluate the current water chemistry of lakes and streams, determine the status of fisheries and other biotic resources, and select regionally representative surface waters for a long-term monitoring program to study changes in aquatic resources. A synoptic survey of eastern lakes is part of the first phase of the National Surface Water Survey lake study. This manual delineates the quality assurance plan for the Eastern Lake Survey-Phase I.

To ensure that procedures are performed consistently and that the quality of the data generated can be determined, the Quality Assurance Project Plan for the Eastern Lake Survey-Phase I specifies the following measures:

- Provide detailed, written sampling methodology.
- Simultaneously train all personnel participating in field activities.
- Conduct site visits to each field operations base throughout the sampling period to ensure that all methods are being performed properly.
- Perform extensive evaluation of analytical laboratories both before selection and throughout their participation.
- Assess variability introduced at each level of activity in both field and analytical laboratories by processing audit samples (both synthetic and natural lake samples), duplicates, and blanks along with routine samples.
- Provide detailed, written analytical methodology.
- Use internal quality control procedures at the field and analytical laboratories to detect potential contamination and to verify established detection limits.
- Enforce holding time requirements.
- Use protocols in the field and in the analytical laboratory to confirm that reported data are correct.
- Enter data into the data base twice, and scan for outlying values to eliminate effects of transcription errors.

- Verify data by means of range checks, internal consistency checks, and quality assurance evaluations.

- Validate verified data by analysis of the reasonableness of data; base the analysis on the values expected for the particular region or subregion involved.

ACKNOWLEDGMENT

Contributions provided by the following individuals were essential to the completion of this quality assurance document and are gratefully acknowledged: R. Linthurst, R. Schonbrod (U.S. Environmental Protection Agency); J. Baker, J. Engels, M. Faber, J. Fountain, Jr., D. Hoff, F. Morris, D. Peck, J. Potter, M. Stepanian (Lockheed Engineering and Management Services Company, Inc.); J. Kramer (McMaster University); J. Eilers (Northrop Services, Inc.); D. Landers (State University of New York); D. Brakke (Western Washington University); and the word processing staff at Computer Sciences Corporation.

NATIONAL SURFACE WATER SURVEY - EASTERN LAKE SURVEY
(PHASE I -- SYNOPTIC CHEMISTRY)
QUALITY ASSURANCE PLAN

TABLE OF CONTENTS

Section		Page	Revision
1.0	INTRODUCTION	1 of 3	6
2.0	PROJECT DESCRIPTION	1 of 3	6
3.0	PROJECT ORGANIZATION	1 of 4	6
4.0	QUALITY ASSURANCE OBJECTIVES FOR PRECISION, ACCURACY, COMPLETENESS REPRESENTATIVENESS, AND COMPARABILITY	1 of 4	6
4.1	Precision and Accuracy	1 of 4	6
4.2	Completeness	4 of 4	6
4.3	Representativeness	4 of 4	6
4.4	Comparability	4 of 4	6
5.0	SAMPLING STRATEGY	1 of 5	6
5.1	Selection of Sampling Design	1 of 5	6
5.2	Allocation of Lakes within Strata	5 of 5	6
5.3	Number of Samples per Lake	5 of 5	6
6.0	FIELD OPERATIONS	1 of 21	6
6.1	Helicopter Crew Activities	1 of 21	6
6.2	Field Station Operations	8 of 21	6
6.3	Training	18 of 21	6
7.0	FIELD MEASUREMENT QUALITY CONTROL CHECKS	1 of 5	6
7.1	Lake Site Measurements	1 of 5	6
7.2	Field Laboratory Measurements	2 of 5	6
8.0	ANALYTICAL PROCEDURES	1 of 2	6
9.0	ANALYTICAL INTERNAL QUALITY CONTROL	1 of 17	6
9.1	Sample Receipt	1 of 17	6
9.2	Sample Analysis	1 of 17	6

TABLE OF CONTENTS (Continued)

Section		Page	Revision
9.3	Analytical Laboratory Documentation for Quality Control	1 of 17	6
9.4	Internal Quality Control within Each Method	3 of 17	6
9.5	Overall Internal Quality Control. . .	11 of 17	6
9.6	Instrumental Detection Limits	13 of 17	6
9.7	Data Reporting.	15 of 17	6
9.8	Daily Evaluation of Quality Control Data.	15 of 17	6
10.0	PERFORMANCE AND SYSTEM AUDITS	1 of 5	6
10.1	Performance Audit Samples	1 of 5	6
10.2	Quality Assurance System Audits (On-Site Evaluations)	4 of 5	6
11.0	ACCEPTANCE CRITERIA	1 of 3	6
11.1	Audit Sample Results.	1 of 3	6
11.2	Duplicate Analysis Results.	3 of 3	6
11.3	Corrective Action	3 of 3	6
12.0	DATA MANAGEMENT SYSTEM.	1 of 8	6
12.1	Raw Data Set.	1 of 8	6
12.2	Verified Data Set	1 of 8	6
12.3	Validated Data Set.	7 of 8	6
13.0	DATA EVALUATION AND VERIFICATION.	1 of 6	6
13.1	Field Data Review	1 of 6	6
13.2	Analytical Data Review.	1 of 6	6
14.0	DATA VALIDATION	1 of 9	6
14.1	Overview.	1 of 9	6
14.2	Detection of Outliers	1 of 9	6
14.3	Detection of Systematic Error	7 of 9	6
14.4	Treatment of Outliers and Systematic Differences.	7 of 9	6

TABLE OF CONTENTS (Continued)

Section	Page	Revision
15.0 REFERENCES.	1 of 3	6
APPENDICES		
APPENDIX A - Data Forms for Reporting Analytical Results	1 of 17	6
APPENDIX B - Telephone Record Log	1 of 6	6
APPENDIX C - Field On-Site Evaluation Questionnaire.	1 of 18	6
APPENDIX D - Analytical Laboratory On-Site Evaluation Questionnaire . .	1 of 54	6
APPENDIX E - Eastern Lake Survey Preaward Scoring Sheet.	1 of 4	6
APPENDIX F - Eastern Lake Survey Data Package Completeness Checklist.	1 of 3	6
APPENDIX G - Eastern Lake Survey Verification Report.	1 of 13	6

FIGURES

Figures		Page	Revision
2.1	Organizational diagram of the National Surface Water Survey and approximate years when the field activities are to be initiated	2 of 3	6
3.1	National Surface Water Survey internal management structure	2 of 4	6
5.1	Regions and subregions of the eastern U.S. potentially susceptible to acidic deposition.	4 of 5	6
6.1	Flowchart of helicopter crew activities . .	2 of 21	6
6.2	National Surface Water Survey Form 1 - Lake Data	4 of 21	6
6.3	Field sample label.	7 of 21	6
6.4	Flow scheme of daily field station activities.	9 of 21	6
6.5	Aliquot and audit sample labels	11 of 21	6
6.6	National Surface Water Survey Form 2 - Batch QC Field Data	13 of 21	6
6.7	National Surface Water Survey Form 3 - Shipping.	19 of 21	6
6.8	Eastern Lake Survey data flow scheme. . . .	20 of 21	6
12.1	Data management for the Eastern Lake Survey.	2 of 8	6
14.1	Flowchart for data validation process . . .	3 of 9	6

TABLES

Table		Page	Revision
1.1	Sections in This Report and in the Analytical Methods Manual that Address Quality Assurance Subjects	3 of 3	6
4.1	Quality Assurance Objectives for Precision, Accuracy, and Detectability	2 of 4	6
5.1	Variables Selected for Lake Classification, Eastern Lake Survey	2 of 5	6
6.1	List of Data Forms and Labels Used in the Field	5 of 21	6
6.2	List of Sample Codes	12 of 21	6
6.3	List of Aliquots, Containers, Preservatives, and Corresponding Sample Parameters	14 of 20	6
6.4	Split Sample Descriptions	16 of 20	6
8.1	List of Parameters and Corresponding Measurement Methods	2 of 2	6
9.1	List of Maximum Holding Times	2 of 17	6
9.2	Maximum Control Limits for Quality Control Check Samples (QCCS)	4 of 17	6
9.3	Summary of Internal Quality Control Checks for Analysis Methods	5 of 17	6
9.4	List of Data Forms Used by the Analytical Laboratory	8 of 17	6
9.5	Chemical Reanalysis Criteria	12 of 17	6
9.6	Conductance Factors of Ions	14 of 17	6
9.7	List of Decimal Place Reporting Requirements	16 of 17	6

TABLES (Continued)

Table		Page	Revision
9.8	National Surface Water Survey Lab/Field Data Qualifiers (Tags) . . .	17 of 17	6
10.1	Desired Composition of Synthetic Field and Laboratory Audit Samples for the Eastern Lake Survey.	2 of 5	6
12.1	Data Qualifiers (Flags) for Raw Data Set	3 of 8	6
12.2	Missing Value Codes.	8 of 8	6
13.1	Exception-Generating and Data Review Programs.	3 of 6	6
14.1	Physical Variables Subject to Validation	2 of 9	6
14.2	Pairs of Variables Used to Check for Random and Systematic Errors.	5 of 9	6
14.3	Related Groups of Variables Used in Multivariate Analyses.	6 of 9	6
14.4	External Reference Data Sets Used for Identifying Systematic Differences . .	8 of 9	6

1.0 INTRODUCTION

Data published in earlier studies are consistent with the hypothesis that certain surface waters within the United States have decreased in pH and/or alkalinity over time. Acidic deposition has been suggested as a contributor to such decreases. Also, numerous studies have led to the conclusion that the effects of acidic deposition on surface water chemistry are influenced by variations among lake, stream, and associated watershed characteristics [(U.S. EPA, 1984(a) and (b)].

Attempts have been made to extrapolate local studies to a regional/national scale to estimate quantitatively the risk to aquatic resources (especially fish) from acidic deposition. These assessments have had only limited success because of problems associated with (1) the comparability of the sampling and analytical methodologies used, (2) the possibility of biased or non-representative sampling sites, and (3) a small and incomplete data base.

The National Surface Water Survey (NSWS or "the program") of the National Acid Precipitation Assessment Program (NAPAP), Task Group E (Aquatic Effects) is designed to overcome some of these deficiencies. NSWS is a three-phase program to evaluate the present water chemistry of lakes and streams, determine the status of fisheries and other biotic resources, and select regionally representative surface waters for a long-term monitoring program to study changes in aquatic resources.

A synoptic survey of eastern lakes is part of the first phase of the NSWS lake study. This manual delineates the quality assurance (QA) plan for the Eastern Lake Survey-Phase I (ELS-I) or "the project". A description of the project and its organization is given in the following sections. The planning, thoughts, and decisions that produced the objectives and design of the ELS-I are discussed in detail in U.S. EPA, 1984a and 1984b.

The QA policy of the Environmental Protection Agency (EPA) requires every monitoring and measurement project to have a written and approved QA project plan (Costle, 1979a and 1979b). This requirement applies to all environmental monitoring and measurement efforts authorized or supported by EPA through regulations, grants, contracts, or other formal means. The QA project plan should specify the policies, organization, objectives, functional activities, QA, and quality control (QC) activities designed to achieve the data quality goals of the project. All project personnel should be familiar with the policies and objectives outlined in the QA project plan to assure proper interactions among the field operations, laboratory operations, and data management.

EPA guidance states that the 16 items shown in Table 1.1 should be addressed in the QA project plan (U.S. EPA, 1980). Some of these items are extensively addressed in the methods manual (Hillman et al., 1986) for this project; therefore, as allowed by the guidelines, method-specific discussions are not repeated in this document.

TABLE 1.1. SECTIONS IN THIS REPORT AND IN THE ANALYTICAL METHODS MANUAL THAT ADDRESS QUALITY ASSURANCE SUBJECTS[a]

Subject	This Report	Methods Manual
Title Page		
Table of Contents	T of C	
Project Description	2	
Project Organization and Responsibility	3	
QA Objectives	4	1
Sampling Procedures	6	2
Sample Custody	6	2, 3
Calibration Procedures	6	2
Analytical Procedures	8	4-13
Data Analysis, Validation, and Reporting	6, 9, 12, 13, 14	3
Internal QC Checks	7,9	3
Performance and System Audits	10	
Preventive Maintenance	6	2, 3
Assessment of Precision, Accuracy, and Completeness	4, 11	
Corrective Actions	9, 11	3
QA Reports to Management	9, 10	

[a] Addressing these 16 QA subjects is required by U.S. EPA, 1980.

2.0 PROJECT DESCRIPTION

Figure 2.1 shows the structure of NSWS as presently planned.

The ELS-I portion of NSWS Phase I is a synoptic survey of approximately 1,800 lakes in the Eastern United States. The ELS-I has the following specific objectives:

- Determine the percentage (by number and area) and location of lakes in regions of the Eastern United States that are potentially susceptible to change as a result of acidic deposition and that have low acid-neutralizing capacity (ANC).
- Investigate the relationships among water chemistry, regional acidic deposition patterns, land use, physiographic features, lake morphologic characteristics, and basin geometry, within and among regions of the Eastern United States.
- Identify smaller subsets of representative lakes for more intensive sampling in Phases II (temporal variability and biological resources) and III (long-term monitoring).

ELS-I includes a pilot study that has the following primary objectives:

- Test the statistical sampling design.
- Test all methods that will be used during the survey.
- Finalize the data quality objectives (DQO's) for Phase I.
- Finalize QA/QC guidelines for Phase I.
- Train personnel for the field operations.
- Test the data analysis plan.

To ensure that procedures are performed consistently and that the quality of the data generated can be determined, the QA project plan for ELS-I specifies the following measures:

- Provide detailed, written sampling methodology (Morris et al., 1986).
- Simultaneously train all personnel participating in field activities.

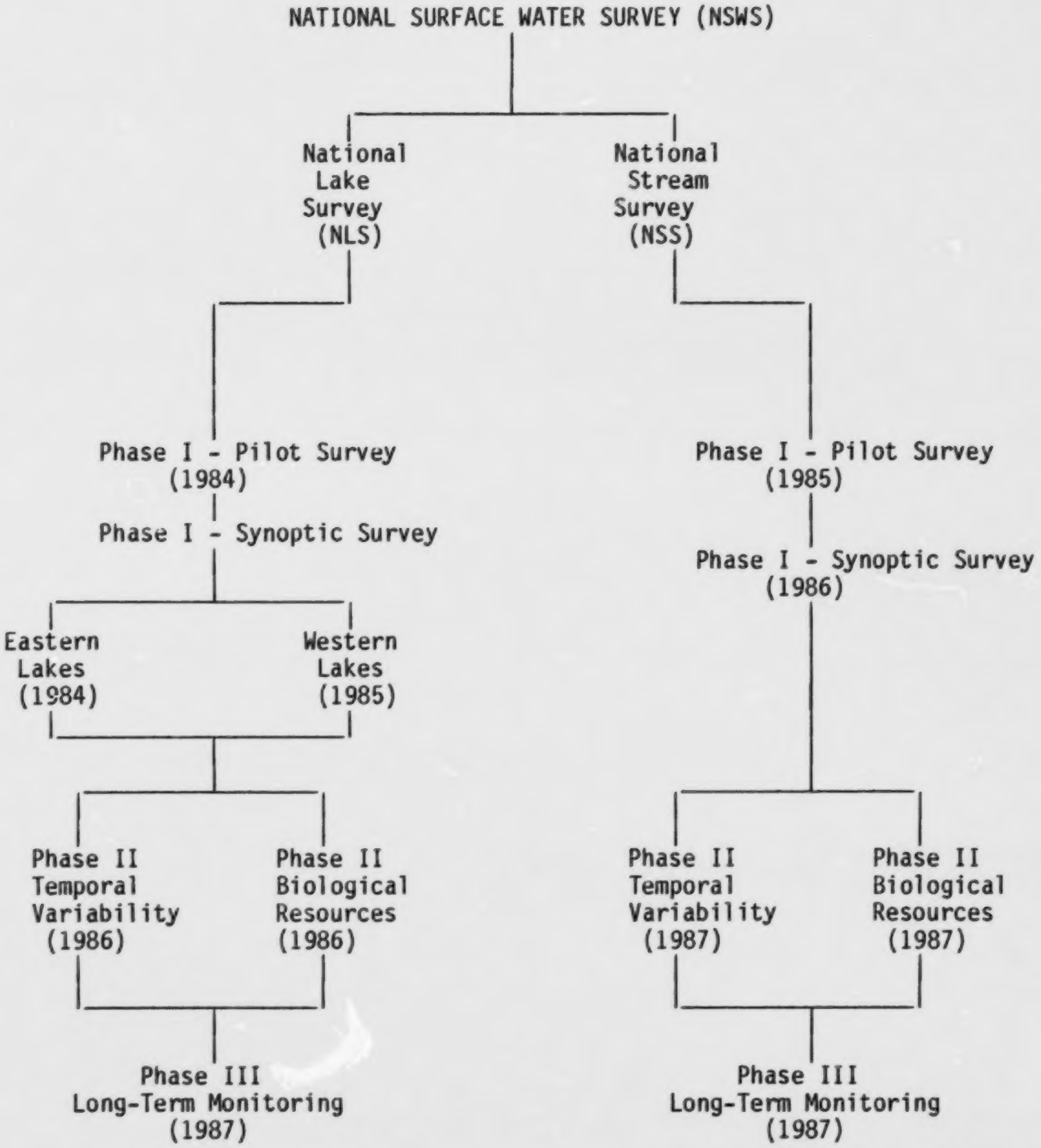

NATIONAL SURFACE WATER SURVEY (NSWS)
National Lake Survey (NLS)
National Stream Survey (NSS)
Phase I - Pilot Survey (1984)
Phase I - Synoptic Survey
Eastern Lakes (1984)
Western Lakes (1985)
Phase II Temporal Variability (1986)
Phase II Biological Resources (1986)
Phase III Long-Term Monitoring (1987)
Phase I - Pilot Survey (1985)
Phase I - Synoptic Survey (1986)
Phase II Temporal Variability (1987)
Phase II Biological Resources (1987)
Phase III Long-Term Monitoring (1987)

Figure 2.1. Organizational diagram of the National Surface Water Survey and approximate years when the field activities are to be initiated.

- Conduct site visits to each field operations base throughout the sampling period to ensure that all methods are being performed properly.

- Perform extensive evaluation of analytical laboratories both before selection and throughout their participation.

- Assess variability introduced at each level of activity in both field and analytical laboratories by processing audit samples (both synthetic and natural lake samples), duplicates, and blanks along with routine samples. (Field laboratory refers to the on-site mobile laboratory that performs preliminary analyses; analytical laboratory refers to the off-site contract laboratory that performs the more sophisticated analyses.)

- Provide detailed, written analytical methodology (Hillman et al., 1986).

- Use internal QC procedures at the analytical laboratory to detect potential contamination and to verify established detection limits.

- Enforce holding time requirements.

- Use protocols in the field and in the analytical laboratory to confirm that reported data are correct.

- Enter data into the data base twice, and scan for outlying values to eliminate effects of transcription errors.

- Verify data by means of range checks, internal consistency checks, and QA evaluations.

- Validate verified data by analyzing the reasonableness of data; base the analysis on the values expected for the particular region or subregion involved.

A quality assurance report describing the findings of the ELS Phase I and the effectiveness of this QA plan will be issued after the completion of Phase I.

3.0 PROJECT ORGANIZATION

Figure 3.1 illustrates the NSWS management structure. The program director is the EPA official who has overall responsibility for the program. The responsibilities of the program manager, technical director, and administrative coordinator are as follows:

Program Manager

The program manager is the EPA Headquarters representative for the NSWS and serves as the liaison between the headquarters staff, the laboratory directors, and NAPAP. Questions regarding general management and resources should be forwarded to the program manager through the technical director.

Technical Director

The technical director performs his responsibilities at the discretion of the program manager. The primary role is to see that the program objectives are satisfied, that the components of the program are well-integrated, and that deadlines are met. The technical director coordinates and integrates the activities of the Environmental Research Laboratory (ERL) at Corvallis, Oregon, the Environmental Monitoring Systems Laboratory (EMSL) at Las Vegas, Nevada, and the Oak Ridge National Laboratory (ORNL) at Oak Ridge, Tennessee. The technical director also coordinates peer review and resolves issues of responsibility. His office is the focal point of general public inquiry and distribution of report information. The technical director represents the program manager as necessary and keeps the program manager informed of EPA laboratory activities, progress, and performance.

Administrative Coordinator

The administrative coordinator reports directly to the program manager. The primary role of this position is to monitor the budget and personnel needs of the survey staff. The administrative coordinator also makes contractual arrangements at the headquarters level and provides special services as needed.

The roles of the various laboratories are as follows:

ERL Corvallis

In view of the role the Corvallis laboratory plays in the Agency's acidic deposition research program, and the major roles it must

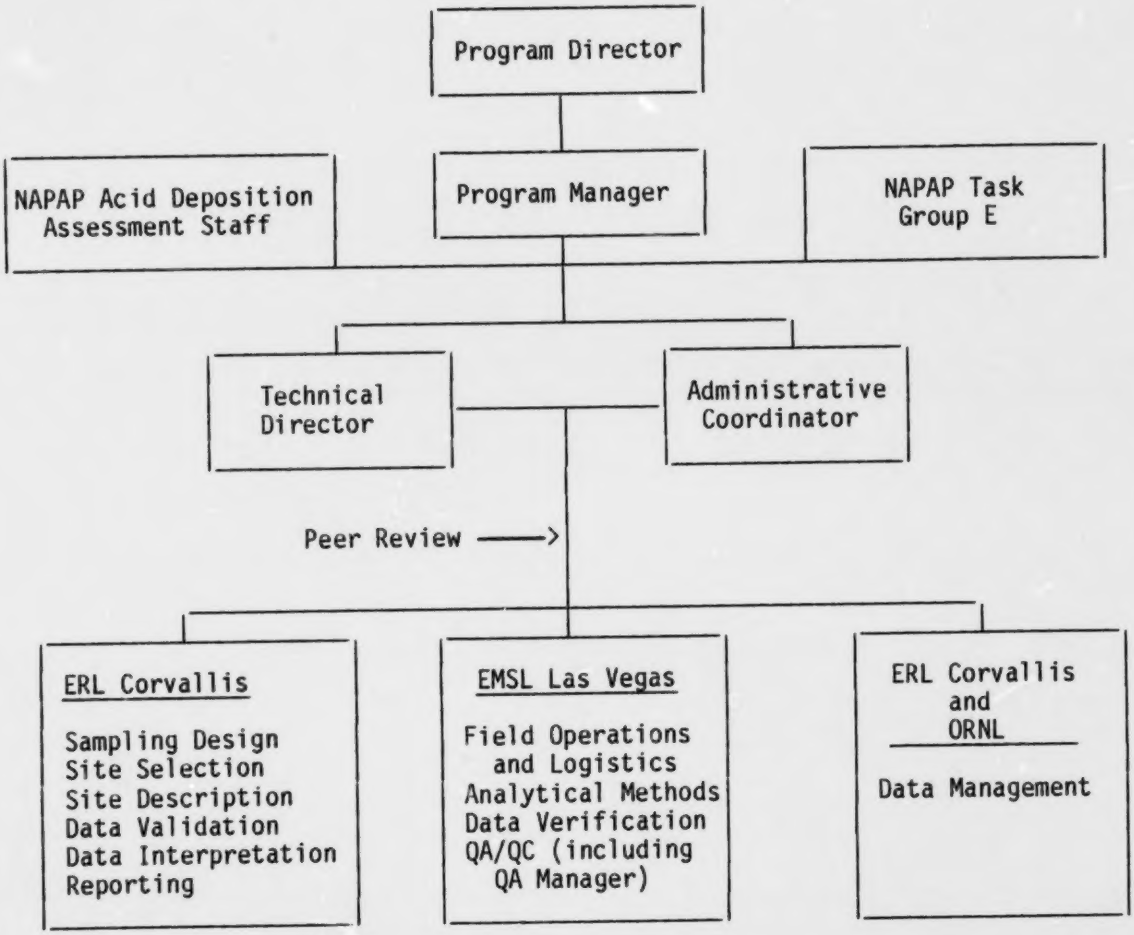

Program Director
NAPAP Acid Deposition Assessment Staff
Program Manager
NAPAP Task Group E
Technical Director
Administrative Coordinator
Peer Review
ERL Corvallis
Sampling Design
Site Selection
Site Description
Data Validation
Data Interpretation
Reporting
EMSL Las Vegas
Field Operations and Logistics
Analytical Methods
Data Verification
QA/QC (including QA Manager)
ERL Corvallis and ORNL
Data Management

Figure 3.1. National Surface Water Survey internal management structure.

perform during the survey program, it is appropriate that ERL Corvallis becomes a primary focal point for ELS-I. Its responsibilities for all phases of NSWS include:

- developing sampling design
- selecting sampling sites
- preparing sampling protocols (jointly with EMSL-LV)
- collecting supplemental historical and other available data on each sample site (aquatic and terrestrial components)
- analyzing data (jointly with EMSL-LV)
- interpreting and mapping data
- preparing reports (final and progress reports, with contributions from the other laboratories relative to their responsibilities)
- assessing and resolving all science-related issues other than QA/QC and data management (jointly with other laboratories as necessary)
- coordinating survey activities with NAPAP management staff.

EMSL Las Vegas

The Las Vegas laboratory has particular expertise in matters relating to QA/QC, logistics, analytical services, and sampling protocols. The responsibilities of this laboratory, for all phases of NSWS, include:

- developing QA/QC procedures for all components of the program, except data management (a responsibility of ORNL and ERL Corvallis)
- preparing all sampling protocols (jointly with ERL Corvallis)
- preparing an analytical methods manual
- preparing a field training and operations manual
- preparing and implementing the QA project plan
- coordinating logistical support and equipment needs for all field operations
- training sampling personnel

- distributing all samples to analytical laboratories
- developing and implementing QA/QC procedures for verifying all field measurements and analytical laboratory data
- independently assessing field measurements and laboratory data quality (bias and variability)
- assessing and resolving all problems pertaining to QA/QC, logistics, and analytical services.

ORNL

ORNL has considerable expertise in managing large data bases, manipulating data, and restructuring data bases to satisfy data analysis needs. ERL Corvallis oversees the activities of ORNL, which has NSWS responsibilities for:

- developing and maintaining a data management system
- entering all field, laboratory, and support data into the data base, and simultaneously assuring data quality
- preparing computer-generated summary tables, statistics, and graphics for reports.

4.0 QUALITY ASSURANCE OBJECTIVES FOR PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS, AND COMPARABILITY

4.1 Precision and Accuracy

The QA objectives for precision and accuracy of the parameters being measured are given in Table 4.1. Precision and accuracy are determined by analyzing data from QA/QC samples. External QA/QC samples include the following:

- Field blank - A field blank is a deionized water sample meeting specifications for ASTM Type 1 reagent water (ASTM, 1984) that is carried to the lake on the helicopter and processed through the Van Dorn sampler as though it were a routine sample. One field blank is collected by each helicopter on each operating day. Field blank data are used to establish the estimated system decision limit, quantitation limit, or background value that can be expected for each type of analysis. For data interpretation, a data point above this value is considered a positive response.

- Field duplicate - A field duplicate is a second sample collected at the lake site by the same team immediately after the routine sample is collected. Field duplicate data are used to estimate the overall within-batch precision for the sampling and analysis process. One field duplicate is collected per field station per operating day.

- Audit samples - Audit samples are materials with known characteristics, used to determine the accuracy of the measurement system. Two types of audit samples serve as QA checks for the ELS-I: field audit samples (both natural and synthetic) help to check the overall field and laboratory performance; laboratory audit samples help to check the performance of the analytical laboratory. Audit samples are discussed in Section 10.0.

Internal field QA/QC samples are used primarily by the sampling teams and field laboratory staff to check the accuracy of the measurement system in the field. Internal field QA/QC samples include the following: Hydrolab QCCS, field laboratory QCCS (for pH, DIC, and turbidity), trailer duplicate, and trailer (calibration) blank. These are described in Sections 6 and 7.

Internal laboratory QA/QC samples include the following: calibration blank, reagent blank, quality control check sample (QCCS), detection limit QCCS, matrix spike, and analytical laboratory duplicate. These are described in Section 9.0.

TABLE 4.1. QUALITY ASSURANCE OBJECTIVES FOR PRECISION, ACCURACY, AND DETECTABILITY

Parameter[a]	Units	Expected Range[b]	Required Detection Limits	Precision Relative Standard Deviation (RSD) Upper Limit (%)[c]	Accuracy Maximum Absolute Bias (%)
Al, Total extractable	mg/L	0.005-1.0	0.005	10 (>0.01) 20 (≤0.01)	10/20
Al, Total	mg/L	0.005-1.0	0.005	10 (>0.01) 20 (≤0.01)	10/20
Acidity (BNC)[d]	µeq/L	10-150	5	10	10
Alkalinity (ANC)[e]	µeq/L	-100-1,000	5	10	10
Ca	mg/L	0.5-20	0.01	5	10
Cl^-	mg/L	0.2-10	0.01	5	10
True Color	Color units[f]	0-200	0	±5[g]	--
DIC	mg/L	0.05-15	0.05	10	10
DOC	mg/L	0.1-50	0.1	5 (>5) 10 (≤5)	10
F^-, Total	mg/L	0.01-0.2	0.005	5	10
Fe	mg/L	0.01-5	0.01	10	10

(continued)

---

[a] Dissolved ions and metals are being determined, except where noted.
[b] Ranges are for lake waters.
[c] Unless otherwise noted, this is the RSD at concentrations above (about 10 times) instrumental detection limits.
[d] BNC = base-neutralizing capacity (∿ acidity)
[e] ANC = acid-neutralizing capacity (∿ alkalinity)
[f] APHA platinum-cobalt units
[g] Absolute precision goal in terms of applicable units.

TABLE 4.1. (Continued)

Parameter[a]	Units	Expected Range[b]	Required Detection Limits	Precision Relative Standard Deviation (RSD) Upper Limit (%)[c]	Accuracy Maximum Absolute Bias (%)
K	mg/L	0.1-1	0.01	5	10
Mg	mg/L	0.1-7	0.01	5	10
Mn	mg/L	0.01-5	0.01	10	10
Na	mg/L	0.5-7	0.01	5	10
NH_4^+	mg/L	0.01-2	0.01	5	10
NO_3^-	mg/L	0.01-5	0.005	10	10
pH, Field	pH units	3-8	---	±0.1 pH[g]	(±0.1)
pH, Analytical lab	pH units	3-8	---	±0.05 pH[g]	(±0.1)
P, Total	mg/L	0.005-0.07	0.002	10 ($P > 0.01$) 20 ($P \leq 0.01$)	10/20
SiO_2	mg/L	2-25	0.05	5	10
SO_4^{2-}	mg/L	1-20	0.05	5	10
Specific Conductance	µS/cm	5-1000	h	1	5
Turbidity	NTU	2-15	2	10	10

[a] Dissolved ions and metals are being determined, except where noted.
[b] Ranges are for lake waters.
[c] Unless otherwise noted, this is the RSD at concentrations above (about 10 times) instrumental detection limits.
[g] Absolute precision goal in terms of applicable units.
[h] Blank must be ≤ 0.9 µS/cm.

4.2 Completeness

The objective for completeness of data (the amount of valid data obtained from a measurement system compared to the amount expected to be obtained under correct normal conditions) is 90 percent or better for all parameters. This figure is based on experience gained during previous studies and is subject to change as experience is gained during the survey.

4.3 Representativeness

The question of representativeness is an important one. ELS-I is designed to achieve the objectives outlined in Section 2. It is not intended to determine the chemistry of any given lake in detail. Therefore, achieving ELS-I objectives does not require that the only sample taken from a lake be completely representative of those waters. In most cases, only one sample per lake will be taken during Phase I. However, a determination of whether one sample per lake is sufficient to achieve the objectives of Phase I can only be made when estimates of "within lake" and "among lakes" variances are obtained. Estimates of these variances will be made using currently available data and the statistical sampling design for Phase I, which will be modified if necessary. (See Section 5.) In Phases II and III, more intensive studies of individual lakes will be performed.

4.4 Comparability

Comparability is assured by having a uniform set of procedures for all sampling teams and a uniform set of units for reporting the data. Furthermore, the QA procedures described in succeeding sections allow for the determination of bias for each sampling team and analytical laboratory so that their results can be compared.

5.0 SAMPLING STRATEGY

The sampling strategy for selecting lakes is outlined here in some detail because the usefulness of the results obtained in this program depends critically on the sampling design. A more complete treatment is given elsewhere (U.S. EPA, 1984c).

The overall strategy is to use a systematic, stratified design to select the lakes. There are three stratification factors: regions, subregions, and alkalinity map classes (Table 5.1). Each stratum is an alkalinity map class within a subregion within a region. All three alkalinity map classes are found within each of the eleven subregions, so the total number of strata in the ELS-I is 33. Within strata, lakes are selected systematically on the basis of geographic location; ordering factors (elevation or lake type) were also used in some strata.

The division of a heterogeneous population into more homogeneous subdivisions can result in a gain in precision over simple random sampling. A systematic approach was chosen over proportional sampling since it is easier to implement and provides similar results.

The stratified systematic sampling design has the following important attributes and advantages:

- It provides an unbiased estimate of the distribution of population attributes of interest, such as the number and area of acidic lakes and low-alkalinity lakes in regions potentially susceptible to acidic deposition.
- It permits comparisons of variable distributions among major strata.
- It can be completed and implemented expeditiously.
- It provides a sound basis for the selection of representative lakes for Phase II and Phase III studies.

5.1 Selection of Sampling Design

The rationale for the choice of the particular stratification and ordering factors are discussed in Sections 5.1.1 and 5.1.2, respectively.

5.1.1 Stratification Factors - The stratification factors are regions, subregions, and alkalinity map classes.

TABLE 5.1. VARIABLES SELECTED FOR LAKE CLASSIFICATION, EASTERN LAKE SURVEY

Level or Criterion	Divisions within Levels or Criteria
Region[a]	1. Northeast 2. Upper Midwest 3. Southeast
Subregion	See Figure 5.1[b,c,d]
Alkalinity Map Class	<100 µeq/L 100 to 200 µeq/L >200 µeq/L
Elevation (used only in 1A and 1C)	<1,200 m (300 m increments) >1,200 m (600 m increments)
Lake Type (used only in 1E and 2A)	Seepage Non-Seepage Reservoir

[a] Regions of interest are defined primarily from alkalinity maps using existing data.

[b] Northeastern subregions: 1A, Adirondack Mountains; 1B, Pocono and Catskill Mountains; 1C, Central New England; 1D, Southern New England; 1E, Maine.

[c] Upper Midwestern subregions: 2A, Northeastern Minnesota; 2B, Upper Peninsula of Michigan; 2C, North-Central Wisconsin; 2D, Upper Great Lakes Area.

[d] Southeastern subregions: 3A, Southern Blue Ridge Mountains; 3B, Florida.

Regions - It is known a priori that certain regions of the United States contain an abundance of low-alkalinity waters and are, therefore, considered potentially susceptible to acidic deposition. Only lakes greater than four hectares in area within those regions were selected for sampling. Three regions were identified and are listed in Table 5.1.

Subregions - Within each region, sufficient data are available to suggest that because of physiography or known water quality information, some areas of each region include lakes that are more similar to each other than to lakes in surrounding areas. To ensure that a representative sample is drawn from each apparently discontinuous portion of the region, subregion was chosen as the second stratification factor. Each subregion is shown in Figure 5.1.

Alkalinity Map Classes - Within each subregion there are lakes with differing alkalinities. Because it is important in this national assessment to refine estimates of the number of lakes in different alkalinity/potential susceptibility classes, the third stratification factor, alkalinity, was incorporated. This choice ensures that samples are collected from a wide range of lakes presently expected to have different chemical compositions. The three alkalinity classes selected are given in Table 5.1. Figures 6.3 through 6.5 in U.S. EPA, 1984(c) show the alkalinity patterns for various regions and subregions, based on currently available data. Alkalinity classes can be obtained from maps prepared by staff at ERL Corvallis (Omernik and Powers, 1985; Omernik and Griffith, 1985; Omernik and Kinney, 1985; Omernik et al., in preparation).

5.1.2 Ordering Factors - The four ordering factors evaluated were elevation, lake type, watershed size, and lake size. Only the first two were used for ordering, and only one per stratum. (See Table 5.1.)

Elevation - Studies in the mountainous parts of the eastern and western United States have demonstrated that water chemistry is correlated with elevation; some of the lowest-alkalinity waters, for example, are found at the highest elevations. Therefore, elevation was selected as an ordering factor.

Lake Type - There are two chemically significant divisions of lake type: seepage (no inlets or outlets) and non-seepage systems. The two types have generally different chemistries and thus could have different responses to potential acidic deposition inputs. Reservoirs have been chosen as a lake-type class to ensure that the data can be used to address regional concerns over drinking water supplies.

Sources for determining lake type and elevation are topographic maps. In general, the 1:250,000 scale U.S. Geological Survey topographic maps are the most practical.

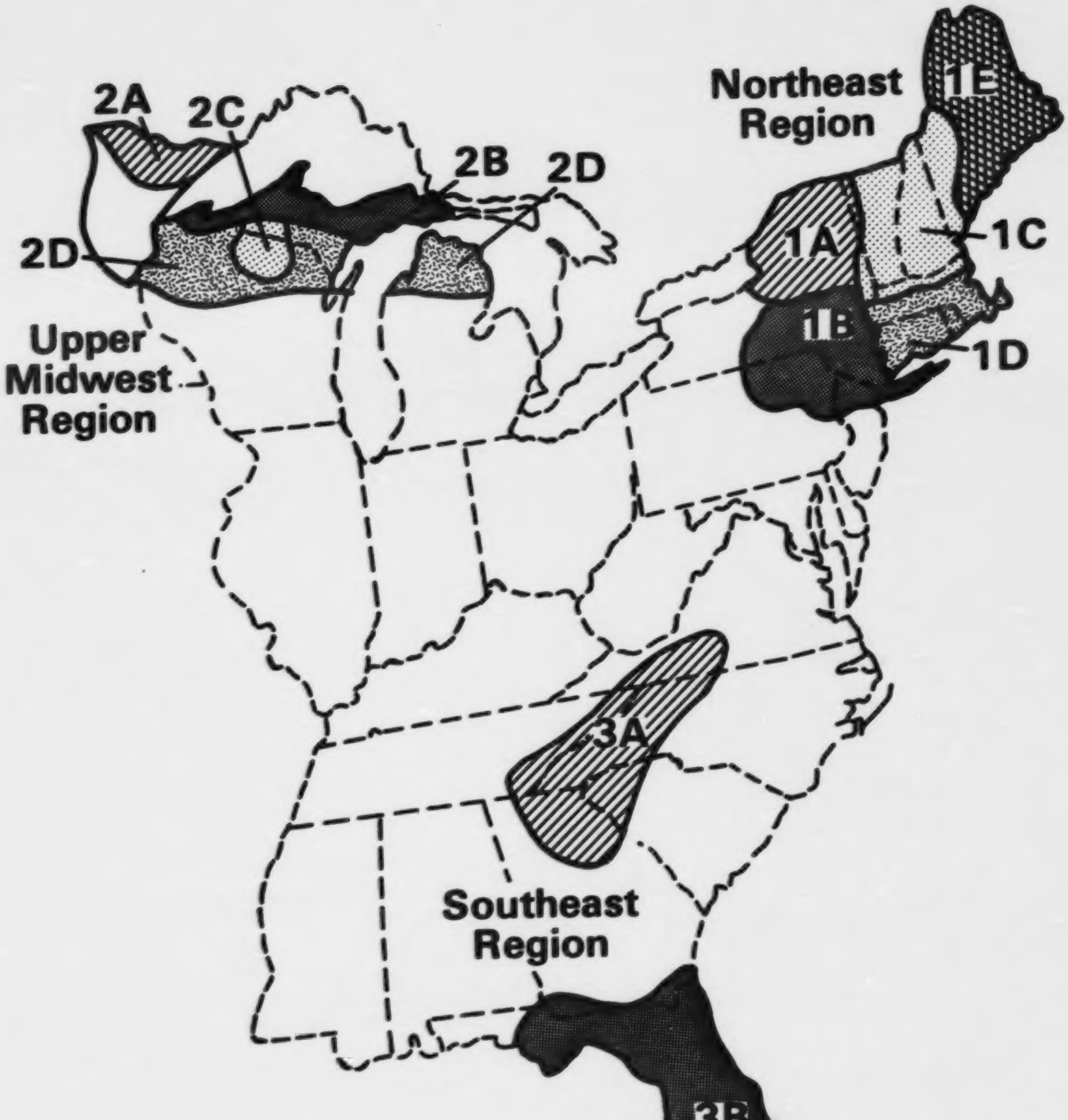

2A
2C
2B
2D
2D
Upper Midwest Region
Northeast Region
1E
1A
1C
1B
1D
3A
Southeast Region
3B

Figure 5.1. Regions and subregions of the eastern United States potentially susceptible to acidic deposition.

5.2 Allocation of Lakes within Strata

Generally, 50 lakes are sampled in each stratum. However, up to 90 lakes per stratum may be chosen in particularly heterogeneous areas or in areas highly susceptible to acidic deposition. In strata represented by fewer than 50 lakes, all lakes are sampled.

All the lakes in some strata are ordered according to one of the ordering factors. The selection of these variables depends on anticipated features of the subregion in question. After the appropriate ordering factor has been applied, the list of lakes is divided into n intervals, where n is the number of lakes to be selected. The first sample lake is selected at random between lakes one and n. Thereafter, every n^{th} lake is selected. This procedure ensures that each lake of a stratum in the frame list has an equal probability of being included.

5.3 Number of Samples per Lake

The present design involves taking one sample per lake. Phase I sampling takes place during the autumn mixing period, since at that time the lakes should be well-mixed, and the one sample should be representative of the lake water chemistry as a whole. The design is optimized for spatial coverage and intercomparison of lakes because within-lake variability is expected to be less than among-lake variability.

However, an attempt will be made to verify that one sample per lake is adequate. The within-lake variability will be estimated for a number of lakes using previously obtained data for selected parameters. For the pilot study, if the within-lake variability is determined to be large enough to influence the reliability of the predictor, three samples will be collected from different areas of the lake.

6.0 FIELD OPERATIONS

Field operations are based at field stations under the supervision of a field base coordinator. Each station contains a mobile laboratory whose activities are conducted by a five-person team. Two helicopter crews operate from each station and make one or more excursions to lake sites each day. On each excursion, 5 to 10 lakes are sampled. The total sample load is restricted to 20 lake samples per station per day.

In the following two sections, the activities of the helicopter crews and field station crews are discussed. A more detailed description of field operations (including safety) is given in Morris et al., 1986. Section 6.3 of this QA project plan addresses the field personnel training.

6.1 Helicopter Crew Activities

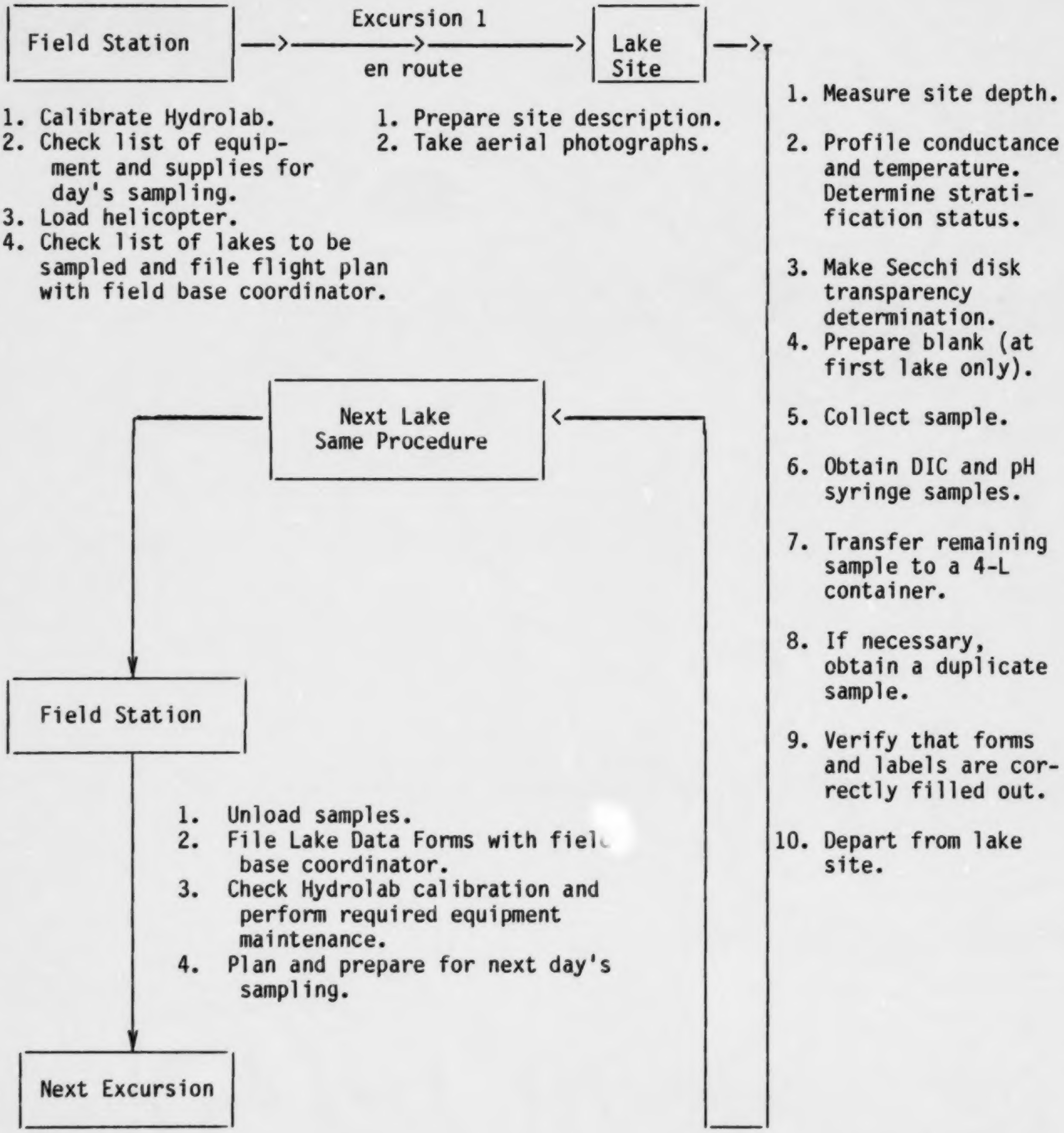
Each helicopter crew consists of a pilot, an observer, and a sampler. The observer's responsibility is to ensure that all measurements and sampling operations are performed correctly and that data are accurately recorded. The sampler must be qualified to operate all equipment and follow prescribed procedures. For each excursion, the activities of each helicopter crew are divided into (1) activities at the field station and (2) activities en route to or at the lake site. They are described in the following two subsections. A flow chart of field crew activities is shown in Figure 6.1.

6.1.1 Station Activities - Prior to leaving the field station, helicopter crews perform the following tasks:

- Prepare a detailed navigation sheet giving courses and distances for the excursion as well as the navigational coordinates of each lake to be sampled. A flight plan is filed with the field base coordinator in order to predict when samples will arrive and for safety considerations. Preliminary information about a lake, such as latitude, longitude, name, and status (regular, alternative, or special), is supplied by ERL Corvallis and local authorities. If possible, the location of the deepest part of each lake is predetermined and indicated on a map as the preferred sampling site.

- Ensure that they have all the required supplies.

- Calibrate the Hydrolab unit, which is used to obtain pH, conductance, and temperature profiles of each lake. The procedures are described in detail in Section 7 of this QA project plan. Hydrolab calibration data are recorded on the Hydrolab calibration form.



Field Station:

1. Calibrate Hydrolab.
2. Check list of equipment and supplies for day's sampling.
3. Load helicopter.
4. Check list of lakes to be sampled and file flight plan with field base coordinator.

En route:

1. Prepare site description.
2. Take aerial photographs.

Lake Site:

1. Measure site depth.
2. Profile conductance and temperature. Determine stratification status.
3. Make Secchi disk transparency determination.
4. Prepare blank (at first lake only).
5. Collect sample.
6. Obtain DIC and pH syringe samples.
7. Transfer remaining sample to a 4-L container.
8. If necessary, obtain a duplicate sample.
9. Verify that forms and labels are correctly filled out.
10. Depart from lake site.

Field Station:

1. Unload samples.
2. File Lake Data Forms with field base coordinator.
3. Check Hydrolab calibration and perform required equipment maintenance.
4. Plan and prepare for next day's sampling.

Figure 6.1. Flowchart of helicopter crew activities.

Once these steps are performed, the helicopter proceeds to the lake to take samples.

6.1.2 Lake Site Activities - As a lake is approached, photographs of the area are taken. Preceding each set of lake photographs, a photo of a card showing the date and the lake identification (ID) number is taken. After the photographs are taken, the photograph numbers are written on Form 1, Lake Data, shown in Figure 6.2. (Table 6.1 lists the data forms and labels used in the field.) The observer also notes watershed characteristics which can be determined from the air. Form 1 contains an outline of the lake, sketched previously from topographic maps. The sampling location is marked on the sketch with an x. The pilot then lands at or near the deepest part of the lake. This point is determined by using a combination of visual observations from the air and the depth recorder.

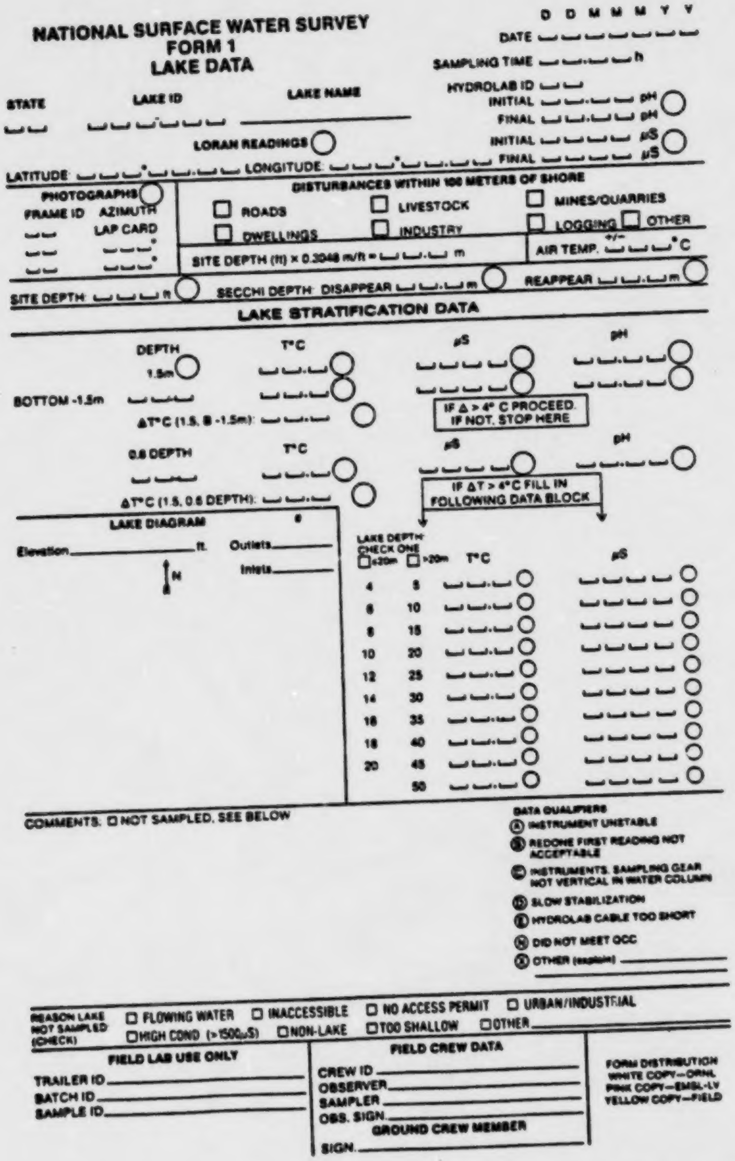
NOTE: Procedures have been developed to handle problem situations that may develop. These situations include finding at the coordinates given: (1) no lake, (2) more than one lake, (3) a stream or flowing water, (4) a lake too shallow to obtain a debris-free water sample (<0.5 m), (5) an inaccessible lake, (6) a lake with high conductance (>1500 µS/cm), (7) a small lake, and (8) a multilobed or dendritic lake for which the location of the best sampling site is uncertain. These procedures are described in detail in Morris et al., 1986.

The following operations are performed in the order given. The pilot maintains position by visual reference to landmarks or an anchored buoy, as conditions dictate.

1. Depth - The lake depth at the sampling site is determined with the electronic depth finder or calibrated sounding line and the result is recorded on Form 1.

2. Parameter Profile - pH, specific conductance, and temperature are measured at 1.5 m below the surface and at 1.5 m above the lake bottom, using the Hydrolab. If the temperature difference exceeds 4°C, a third measurement is obtained at 60 percent of the lake depth. If the temperature difference between the top and 60 percent depth is $\leq$4°C, the lake is classified as weakly stratified. If the temperature difference exceeds 4°C, the lake is considered to be strongly stratified. In a strongly stratified lake, a temperature and conductance profile is obtained at 5 m intervals for lakes greater than 20 m deep and 2 m intervals for lakes less than 20 m deep. The results are recorded on Form 1.

3. Secchi Disk Transparency - A Secchi disk secured on a calibrated



NATIONAL SURFACE WATER SURVEY
FORM 1
LAKE DATA

D D M M M Y Y
DATE
SAMPLING TIME h
HYDROLAB ID
INITIAL pH ○
FINAL pH
INITIAL µS ○
FINAL µS

STATE
LAKE ID
LAKE NAME
LORAN READINGS ○
LATITUDE: °
LONGITUDE: °

PHOTOGRAPHS ○
FRAME ID
AZIMUTH
LAP CARD

DISTURBANCES WITHIN 100 METERS OF SHORE
☐ ROADS ☐ LIVESTOCK ☐ MINES/QUARRIES
☐ DWELLINGS ☐ INDUSTRY ☐ LOGGING ☐ OTHER

SITE DEPTH (ft) × 0.3048 m/ft = m
AIR TEMP. +/− °C

SITE DEPTH: ft ○
SECCHI DEPTH: DISAPPEAR m ○
REAPPEAR m ○

LAKE STRATIFICATION DATA

DEPTH	T°C	µS	pH
1.5m ○	○	○	○
BOTTOM -1.5m	○	○	○

ΔT°C (1.5, B -1.5m): ○

IF Δ > 4° C PROCEED.
IF NOT, STOP HERE

0.8 DEPTH	T°C	µS	pH
	○	○	○

ΔT°C (1.5, 0.8 DEPTH): ○

IF ΔT > 4°C FILL IN FOLLOWING DATA BLOCK

LAKE DIAGRAM
Elevation ft.
Outlets
Inlets
N

LAKE DEPTH: CHECK ONE

☐ <20m	☐ >20m	T°C	µS
4	5	○	○
6	10	○	○
8	15	○	○
10	20	○	○
12	25	○	○
14	30	○	○
16	35	○	○
18	40	○	○
20	45	○	○
	50	○	○

COMMENTS: ☐ NOT SAMPLED, SEE BELOW

DATA QUALIFIERS
Ⓐ INSTRUMENT UNSTABLE
Ⓑ REDONE FIRST READING NOT ACCEPTABLE
Ⓒ INSTRUMENTS, SAMPLING GEAR NOT VERTICAL IN WATER COLUMN
Ⓓ SLOW STABILIZATION
Ⓛ HYDROLAB CABLE TOO SHORT
Ⓝ DID NOT MEET QCC
Ⓧ OTHER (explain)

REASON LAKE NOT SAMPLED (CHECK)
☐ FLOWING WATER ☐ INACCESSIBLE ☐ NO ACCESS PERMIT ☐ URBAN/INDUSTRIAL
☐ HIGH COND (>1500µS) ☐ NON-LAKE ☐ TOO SHALLOW ☐ OTHER

FIELD LAB USE ONLY
TRAILER ID
BATCH ID
SAMPLE ID

FIELD CREW DATA
CREW ID
OBSERVER
SAMPLER
OBS. SIGN.
GROUND CREW MEMBER
SIGN.

FORM DISTRIBUTION
WHITE COPY—ORNL
PINK COPY—EMSL-LV
YELLOW COPY—FIELD

Figure 6.2. National Surface Water Survey Form 1 - Lake Data.

TABLE 6.1. LIST OF DATA FORMS AND LABELS USED IN THE FIELD

Data Form	Description
1	Lake Data
2	Batch QC Field Data
3	Shipping
-	Hydrolab Calibration Form
-	Field Sample Label
-	Field Audit Sample Label
-	Lab Audit Sample Label
-	Aliquot Label

line is lowered on the shady side of the helicopter until the disk disappears from view. The disk is then raised until it reappears. Both of these depths are recorded on Form 1. Their average is the Secchi disk transparency. The observer must not wear sunglasses.

4. Sample Collection - The 6.2-L Van Dorn sampler is rinsed with surface water, lowered to 1.5 m below the lake surface, triggered to collect a sample, raised to the surface, then set on the pontoon platform in a vertical position. This is done to prevent the sample from leaking. It is imperative that air is not introduced before steps 5 and 6 are performed.

   NOTE: Sample collection is performed on the upwind side of the helicopter to minimize contamination potential.

5. DIC and pH Syringe Samples - From the Luer-Lok syringe port on the Van Dorn sampler, a 20-mL aliquot is withdrawn using a 60-mL syringe (equipped with valve). The syringe is rinsed with this aliquot and the rinse is discarded. A 60-mL aliquot is withdrawn and the syringe is sealed. A second syringe sample is obtained similarly. A field sample label, shown in Figure 6.3, is completed and attached. "Batch ID" and "Sample ID" are assigned at the field station. After labeling, the syringes are placed in a plastic bag and are stored in the cooler (maintained at 4°C).

6. Sample Transfer - A clean 4-L Cubitainer is rinsed with three 500-mL portions of sample. The Cubitainer is filled with sample, compressed to remove all headspace, then capped securely. The field sample label shown in Figure 6.3 is attached and completed. After labeling, the Cubitainer is stored in the cooler (maintained at 4°C).

7. Duplicate Sample Collection - At the first lake sampled each day, one or both helicopter crews at each station (as assigned by the field base coordinator) collect a duplicate sample by repeating steps 4 through 6. On the label (Figure 6.3), sample type "Duplicate" is checked.

8. Field Blank Sample Collection - One field blank is prepared on the first excursion of each day. In place of step 4, the Van Dorn sampler is rinsed with three 200-mL portions of deionized water, then is filled with deionized water. Step 6 is performed as for a lake sample. The sample type "Blank" is checked on the label (Figure 6.3).

9. Upon completion of steps 1 through 8, the Hydrolab sonde and the Van Dorn sampler are rinsed with deionized water and are stored securely

<table>
<tr><td>Lake ID
____________</td><td>Crew ID
____________</td></tr>
<tr><td>Date Sampled
____________</td><td>Time Sampled
____________</td></tr>
<tr><td colspan="2">Sample Type (Check One)
Routine ______
Duplicate ______
Blank ______</td></tr>
<tr><td>Batch ID
____________</td><td>Sample ID
____________</td></tr>
</table>

Figure 6.3. Field sample label.

in the helicopter. The observer verifies that the Lake Data Form is properly completed and that all containers are correctly labeled.

10. The helicopter proceeds to the next lake, where the same lake site activities are performed. When time necessitates, the helicopter returns to the field station. The helicopter is refueled, when necessary, at remote airports or by fuel truck. The Hydrolab calibration is checked at the end of each day. Any drift is noted on the calibration form. The manufacturer's instructions for care and maintenance of the pH meter and electrode are followed. The rechargeable batteries are charged overnight and the electrodes are stored in tap water or 3M KCl.

6.2 Field Station Operations

The field station includes a fully equipped mobile laboratory, staffed by a field lab coordinator, a field lab supervisor, and three analysts. The field lab coordinator is responsible for the overall operation of the laboratory (sample tracking and logistics, data, forms, safety, etc.). The field lab supervisor, with the aid of the analysts, is responsible for field station measurements and sample processing. When possible, the field lab coordinator also assists with sample processing. This section describes the field station activities that are outlined in Figure 6.4. Subsection 6.2.1 describes reagent preparation and 6.2.2 describes sample processing.

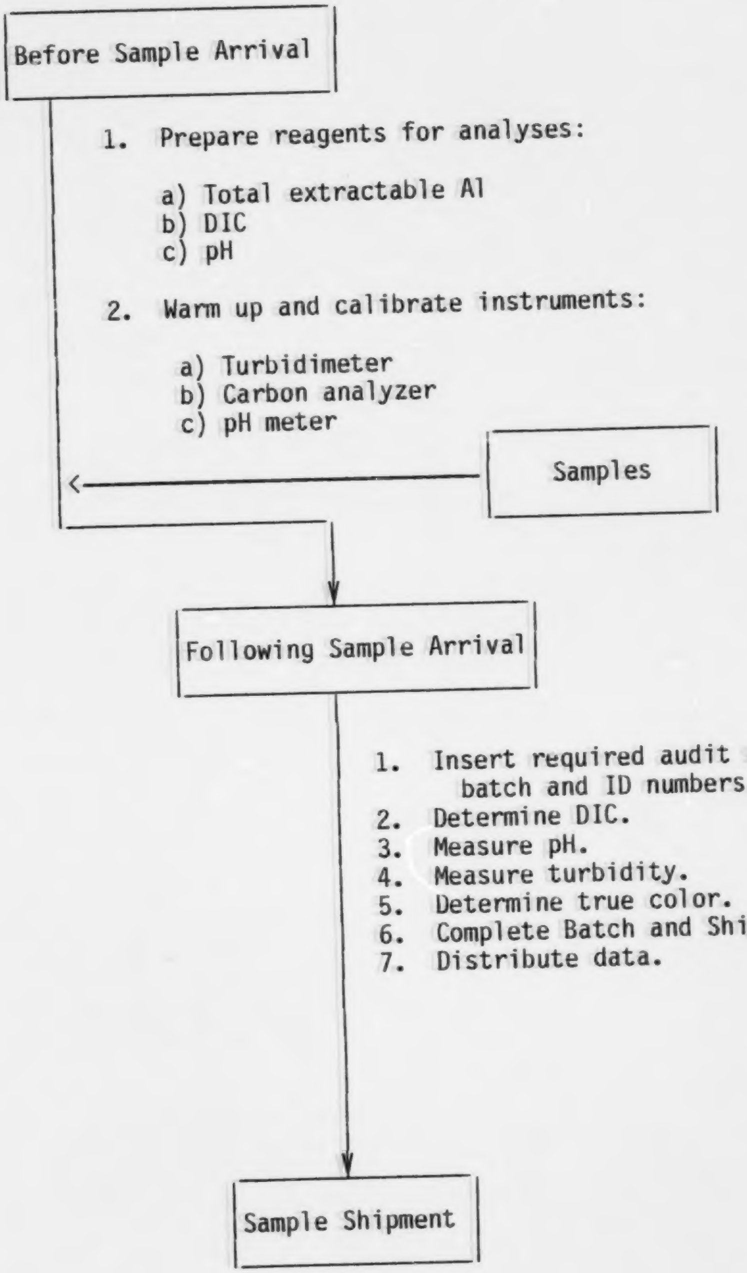
6.2.1 Reagent Preparation - Reagents for aluminum extraction, DIC determination, and pH determination must be prepared before helicopter crews return with samples. Detailed procedures for reagent preparations are given in Morris et al., 1986.

6.2.2 Sample Processing - The following steps describe sample processing operations. They are performed in the order given.

6.2.2.1 Sample Description and Identification -

1. Samples are organized into batches that are processed together. A batch consists of all samples (approximately 20 to 30 including routine, duplicate, blank, split, and audit samples) processed at a field station on a given day. Each batch is assigned a unique batch ID number, which is recorded on the labels of all samples (and of corresponding aliquots). Each sample is then randomly assigned a sample ID number as follows:

   Routine Samples - Three sample containers are filled at each lake, namely two syringes (for DIC and pH determinations) and a Cubitainer. One sample ID number is assigned to all three containers and is recorded on each container label.


Before Sample Arrival
Samples
Following Sample Arrival
Sample Shipment

1. Prepare reagents for analyses:
    - a) Total extractable Al
    - b) DIC
    - c) pH
2. Warm up and calibrate instruments:
    - a) Turbidimeter
    - b) Carbon analyzer
    - c) pH meter

1. Insert required audit samples, assign batch and ID numbers, start Batch Form.
2. Determine DIC.
3. Measure pH.
4. Measure turbidity.
5. Determine true color.
6. Complete Batch and Shipping Forms.
7. Distribute data.

Figure 6.4. Flow scheme of daily field station activities.

Duplicate and Blank Samples - Sample ID numbers are assigned in the same manner as for the routine samples. (Note: There are no syringe samples for the blanks.)

Field Audit Samples - One 2-L field audit sample (received each day from a central source) is included in each day's batch of samples. The label on the field audit container is shown in Figure 6.5a. The code (Table 6.2) indicates what kind of a sample it is and the concentrate lot number. A field audit sample is assigned a sample ID number in the same manner as a routine sample. The ID number is recorded on the label.

Lab Audit Samples - One lab audit sample (received each day from a central source) is included in each day's batch. A single lab audit sample consists of a set of seven aliquots. Each aliquot has a temporary label like that in Figure 6.5b, giving the aliquot number, audit sample code, amount of preservative, and shipping date. An aliquot label (Figure 6.5c) is attached to each aliquot. The lab audit sample is then assigned a sample ID and batch ID number in the same manner as a routine sample. The batch and sample ID numbers are recorded on each of the seven aliquot labels. The date and amount of preservative are also recorded on the label.

After the batch and sample ID numbers are assigned and recorded on each sample label, the same information is entered on Form 2, Batch QC Field Data (Figure 6.6). Also, the lake ID and the appropriate code for each sample (from Table 6.2) are entered on Form 2.

Note 1: The sample ID numbers are assigned at random to all samples in a batch. Furthermore, sample ID numbers run consecutively from 1 to the number of samples in the batch. Audit samples must not always be assigned the same sample ID number.

Note 2: Field audit samples are processed exactly like routine lake samples (steps 1 through 6). Lab audit samples receive no field treatment other than labeling and shipping.

Note 3: Seven different aliquots (numbered as in Table 6.3) are prepared from each field sample (routine, duplicate, and blank samples). Each aliquot is assigned the same batch and sample ID numbers as the sample from which it is prepared. Additional aliquots are taken for split samples.

Note 4: After the lake and sample ID numbers and the sample codes

FIELD AUDIT SAMPLE	
Radian ID No.	
Date Shipped	Date Received
Code	
Batch	ID

a. Field Audit Sample Label

LAB AUDIT SAMPLE	
Aliquot No.	
Date Shipped	Date Received
Code	
Preservative Amount	

b. Lab Audit Sample Label

Aliquot No. ____________

Batch ID ____________

Sample ID ____________

Date Sampled ____________

Preservative ____________

Amount ____________

Parameters ____________

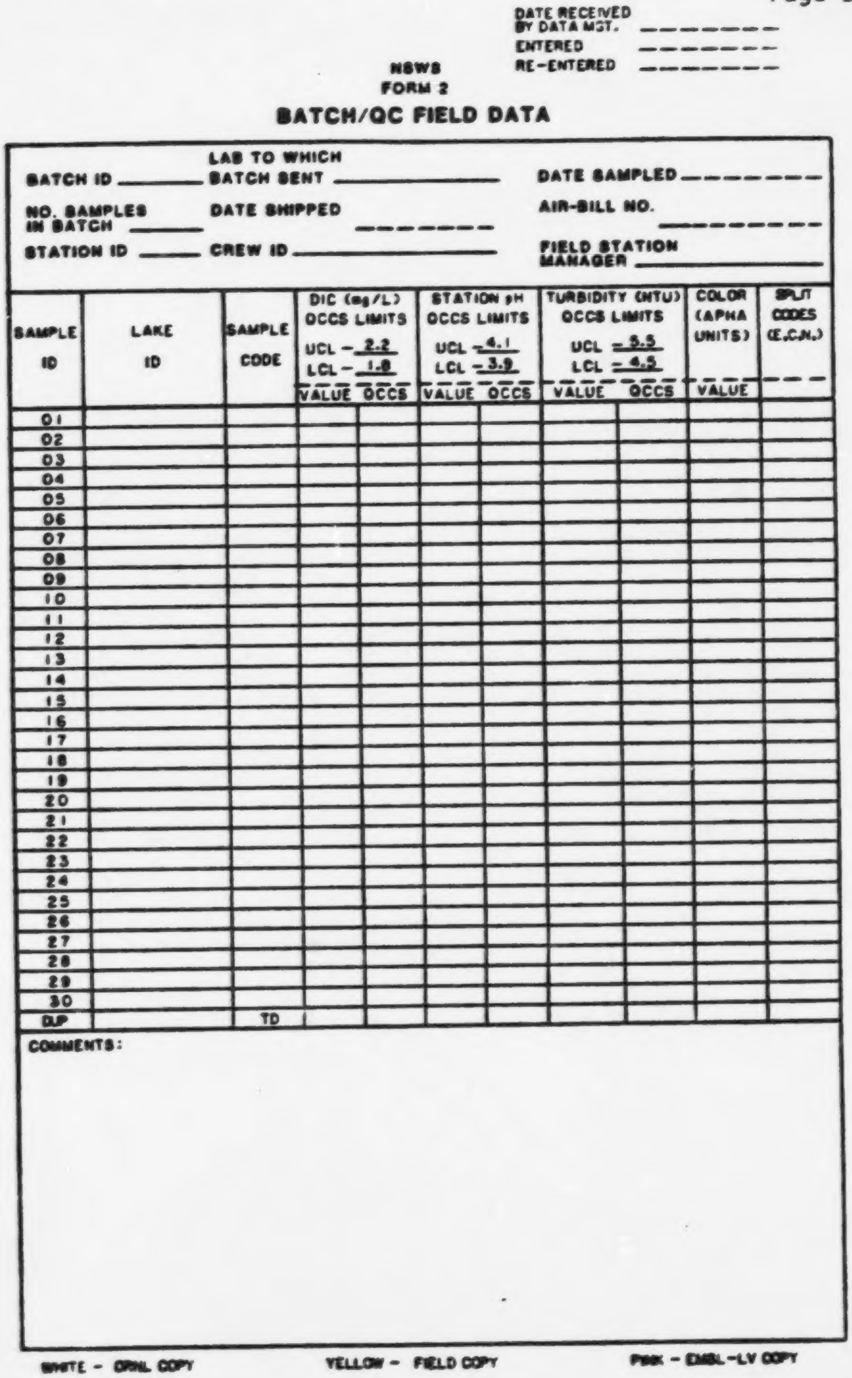
Note: The aliquot no., preservative, and parameters are preprinted on the seven aliquot labels.

c. Aliquot Label

Figure 6.5. Aliquot and audit sample labels.

TABLE 6.2. LIST OF SAMPLE CODES

Sample Type	Code	Description
Normal	R	Routine lake sample
	D	Duplicate lake sample
	B	Field blank sample
	TD	Field station (trailer) duplicate
Audit	F L 1-1	Radian ID number Concentrate lot number Concentration level (L = low, H = high, N = natural) Type of audit sample (F = field audit sample L = lab audit sample P = performance evaluation sample)
Split	E	A split sample is an additional aliquot from a routine, duplicate, or blank sample, and has the same ID number as the original sample. However, the aliquot has an additional sample code. For example, suppose that the original sample is assigned the ID number 4. The split sample also receives the ID number 4, as well as the letter E recorded under the Split Code column on Form 2 (or N or C, depending on where the split sample is shipped). Shipping destination of split sample (N = Norwegian lab, C = Canadian lab, E = EPA Corvallis lab)



DATE RECEIVED BY DATA MGT. ________
ENTERED ________
RE-ENTERED ________

NSWS
FORM 2

BATCH/QC FIELD DATA

BATCH ID ______ LAB TO WHICH BATCH SENT ______________ DATE SAMPLED ________
NO. SAMPLES IN BATCH ______ DATE SHIPPED ________ AIR-BILL NO. ________
STATION ID ______ CREW ID ______________ FIELD STATION MANAGER ______________

SAMPLE ID	LAKE ID	SAMPLE CODE	DIC (mg/L) QCCS LIMITS UCL – 2.2 LCL – 1.8		STATION pH QCCS LIMITS UCL – 4.1 LCL – 3.9		TURBIDITY (NTU) QCCS LIMITS UCL – 5.5 LCL – 4.5		COLOR (APHA UNITS)	SPLIT CODES (E.C.N.)
			VALUE	QCCS	VALUE	QCCS	VALUE	QCCS	VALUE	
01										
02										
03										
04										
05										
06										
07										
08										
09										
10										
11										
12										
13										
14										
15										
16										
17										
18										
19										
20										
21										
22										
23										
24										
25										
26										
27										
28										
29										
30										
DUP		TD								

COMMENTS:

WHITE - ORNL COPY YELLOW - FIELD COPY PINK - EMSL-LV COPY

Figure 6.6. National Surface Water Survey Form 2 - Batch QC Field Data.

TABLE 6.3. LIST OF ALIQUOTS, CONTAINERS, PRESERVATIVES, AND CORRESPONDING SAMPLE PARAMETERS

	Aliquot/(Container)						
	1 (250 mL)	2 (10 mL)	3 (250 mL)	4 (125 mL)	5 (500 mL)	6 (125 mL)	7 (125 mL)
Preservative and Description[a]	Filtered pH <2 with HNO_3	Filtered MIBK-HQ Extract	Filtered No Preservative	Filtered pH <2 with H_2SO_4	Unfiltered No Preservative	Unfiltered pH <2 with H_2SO_4	Unfiltered pH <2 with HNO_3
Parameters	Ca	Total Extractable Al	Cl^-	DOC	pH	Total P	Total Al
	Mg		F^-	NH_4^+	BNC		
	K		SO_4^{2-}		ANC		
	Na		NO_3^-		Specific Conductance		
	Mn		SiO_2		DIC		
	Fe						

[a] Aliquots 2, 3, 4, 5, and 6 must be stored at 4°C in the dark.

are entered on Form 2, the temporary label on the lab audit sample is removed (seven aliquots) and placed in the lab audit logbook.

6.2.2.2 DIC determination - Immediately after assignment of batch and sample ID numbers, one crew member begins the DIC analyses. DIC is determined in routine, lake duplicate, and field audit samples. The routine and lake duplicate samples are contained in sealed syringes (filled at the lake site). For field audit samples, a syringe sample is taken from the 2-L sample prior to analysis. The results are recorded on Form 2, Batch QC Field Data (Figure 6.6). The measurement procedures are discussed in Section 7.2.1. Copies of all raw data must be sent to the QA manager when requested.

6.2.2.3 Sample filtration, preservation, and aliquot preparation - All manipulations are performed in the laminar flow hood by gloved personnel. Sample filtration and preservation are described in Morris et al., 1986. Seven aliquots are prepared from each sample as specified in Table 6.3.

6.2.2.3.1 Split samples - Both Norway and Canada have performed extensive acidic deposition monitoring studies, but each group has used different analytical methodologies. By analyzing the same samples using different methodologies and comparing results, a conclusion can be drawn about the equivalence of Norwegian, Canadian, and ELS-I methods.

There are three types of split samples. Descriptions of each are given below and are summarized in Table 6.4. When a sample is split, the appropriate split code is recorded on Form 2, Batch QC Field Data.

NOTE: These splits are prepared for the ELS-I and may or may not be required for other surveys.

- EPA Corvallis Splits - An EPA Corvallis split consists of one aliquot which is prepared like aliquot 1, except the sample volume is 125 mL and a 125-mL container is used. Volume permitting, all samples are split for Corvallis. When volume limitations exist, sample splits for other laboratories take precedence. Corvallis analyzes the samples by inductively coupled plasma spectroscopy (ICP), providing checks on the performance of the analytical laboratories, as well as additional data that are potentially useful in understanding lake chemistry.
- Norwegian Splits - A Norwegian split consists of one or two aliquots which are identical to aliquot 5. A total of 115 samples from the Northeast will be split to Norway. Ninety of

TABLE 6.4. SPLIT SAMPLE DESCRIPTIONS

Split	Quantity	Number	Descriptions
EPA-Corvallis	125 mL	All samples[a]	Filtered sample acidified with HNO_3 to pH <2
Norwegian[b]	500 mL	90	Raw unfiltered sample
	2x500 mL	25	
Canadian	250 mL[c]	115	Raw unfiltered sample
	250 mL[c]	115	Raw unfiltered sample acidified with HNO_3 to pH <2
	250 mL[d]	115	Raw unfiltered sample
	125 mL[d]	115	Raw unfiltered sample

[a] Except when there is insufficient sample due to other splits
[b] Samples to be taken in the Northeast
[c] Sent to Ontario Ministry of the Environment, Rexdale, Ontario, Canada
[d] Sent to Canada Centre for Inland Waters, Burlington, Ontario, Canada

the splits will consist of one 500-mL aliquot, while twenty-five of the splits will consist of two separate 500-mL aliquots (Norway will return upon receipt one of the two aliquots to the QA manager).

- Canadian Splits - A Canadian split consists of four aliquots, designated as C1, C2, C3, and C4. The aliquots are described below.

C1: Aliquot C1 is identical to aliquot 5 except it consists of 250 mL.

C2: Aliquot C2 is identical to aliquot 7 except it consists of 250 mL.

C3: Aliquot C3 is identical to aliquot 5 except it consists of 250 mL.

C4: Aliquot C4 is identical to aliquot 5 except it consists of 125 mL.

6.2.2.4 Total extractable aluminum - A third crew member begins this procedure at the same time the DIC measurements are begun. The aluminum is extracted into an MIBK layer, which is transferred to a 10-mL centrifuge tube and is capped tightly. An aliquot label (Figure 6.5c) is attached. This is aliquot 2 in Table 6.3. The aliquot is stored at 4°C in the dark until shipment.

6.2.2.5 pH determination (field station) - After DIC determination, the pH of the sample remaining in the sealed syringes is determined. (One syringe should contain about 60 mL sample and the other about 40 mL.) The QC procedures are discussed in Section 7.2.2. The results are recorded on Form 2. Copies of all raw data are sent to the QA manager when requested.

NOTE: Two pH measurements are performed during field operations: (1) in situ at the lake with the Hydrolab and (2) at the field station in a sample chamber.

6.2.2.6 Turbidity - A Monitek Model 21 laboratory nephelometer is used to determine turbidity of routine, duplicate, and blank samples. The nephelometer is calibrated directly in Nephelometric Turbidity Units (NTU). The QC procedures are discussed in Section 7.2.3.

Results are recorded on Form 2. Copies of all raw data are sent to the QA manager when requested.

6.2.2.7 True color determination - After centrifugation to remove turbidity, the color is determined using the Hach Model CO-1 Color Test Kit, following the manufacturer's instructions. Results are recorded on Form 2. The QC procedures are discussed in Section 7.2.4.

6.2.2.8 Sample shipment - When a batch is completely processed and ready for shipment, the samples are assembled into groups according to their shipping destination. Split samples are shipped to ERL Corvallis, to a Canadian lab, or to a Norwegian lab. All other samples are shipped to an analytical lab.

Prior to shipping, each aliquot is sealed in a plastic bag and is placed in a Styrofoam-lined shipping carton, along with 8 to 12 frozen freeze-gel packs to maintain the aliquots at 4°C. One set of Form 3 (Shipping Form, Figure 6.7) is completed for each carton, and two copies (sealed in a plastic bag) are enclosed in the carton. The carton is then sealed and shipped by overnight delivery to its destination.

Upon receiving the shipment, the laboratory checks the temperature and condition of the containers and verifies that all the containers listed on the shipping form are included in the shipment. If there is any discrepancy, the field laboratory coordinator should be notified immediately.

6.2.2.9 Data distribution - Copies of all forms (except labels) are kept at the field station. Copies of Forms 1, 2, and 3 are sent to the locations indicated in Figure 6.8.

One copy of Form 3 is sent to the Sample Management Office (SMO) and two copies are sent with the samples to the analytical lab. Upon receipt by the lab, the condition of the samples is noted on the two forms, one of which is forwarded immediately to SMO.

After the laboratory analysis is completed, the results are entered into the data base by laboratory personnel from a remote terminal, or forms (Appendix A) are sent to the data base manager for entry into the data base. In either case, a copy of the results is sent to the QA manager. Quality assurance of the data transfer into the data base is discussed in Section 12.0.

6.3 Training

Prior to the pilot study and the Phase I survey, all personnel must be trained. Safety procedures and regulations, field base operations, and field laboratory analytical procedures are the chief subjects of instruction. Training includes classes and realistic simulations of actual

NATIONAL SURFACE WATER SURVEY
SAMPLE MANAGEMENT OFFICE
P.O. BOX 818
ALEXANDRIA, VA 22314

NSWS
FORM 3
SHIPPING

RECEIVED BY ____________________
IF INCOMPLETE IMMEDIATELY NOTIFY:
SAMPLE MANAGEMENT OFFICE
(703) 557-2490

PAGE _____ **OF** _____

FROM (STATION ID):	TO (LAB):	BATCH ID	DATE SAMPLED	DATE SHIPPED	DATE RECEIVED
			_______	_______ AIR-BILL NO. _________	_______

SAMPLE ID	ALIQUOTS SHIPPED (FOR STATION USE ONLY)								SPLITS	SAMPLE CONDITION UPON LAB RECEIPT (FOR LAB USE ONLY)
	1	2	3	4	5	6	7	8	9	
01										
02										
03										
04										
05										
06										
07										
08										
09										
10										
11										
12										
13										
14										
15										
16										
17										
18										
19										
20										
21										
22										
23										
24										
25										
26										
27										
28										
29										
30										

QUALIFIERS:
V: ALIQUOT SHIPPED
M: ALIQUOT MISSING DUE TO DESTROYED SAMPLE

Figure 6.7. National Surface Water Survey Form 3 - Shipping.

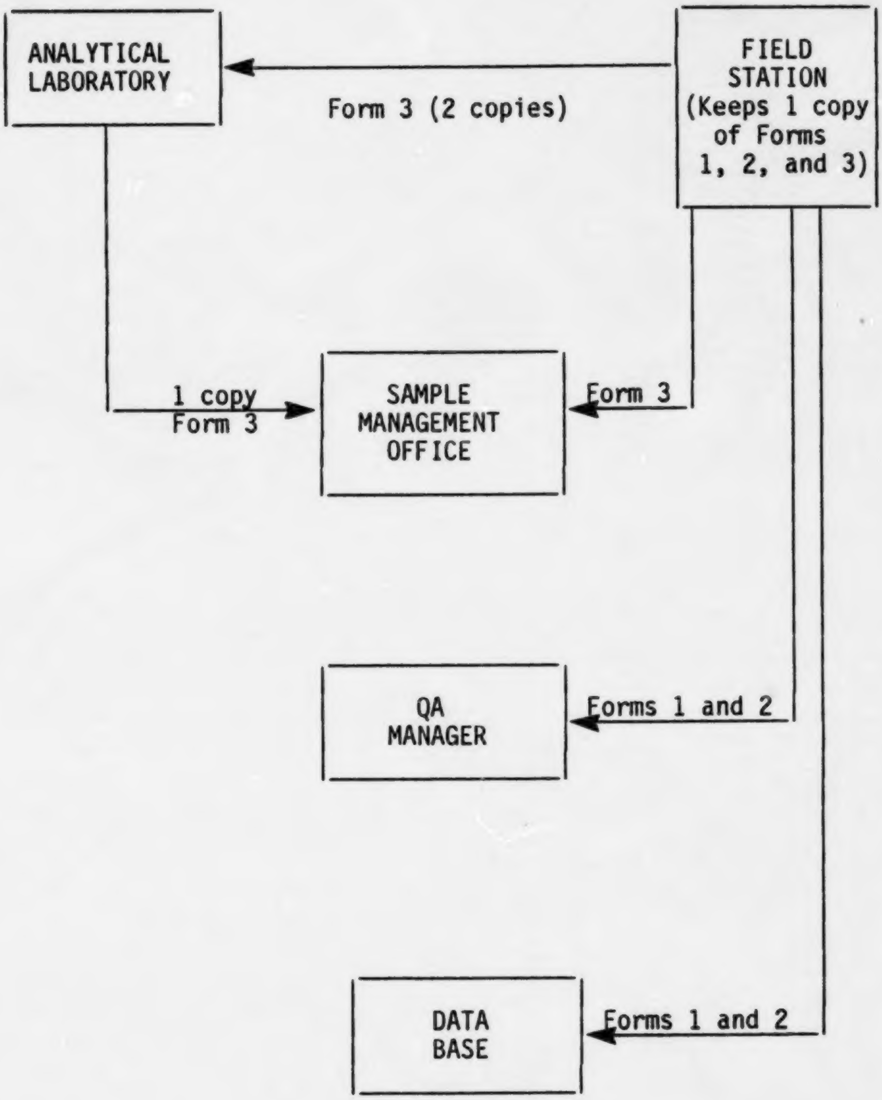

ANALYTICAL LABORATORY
FIELD STATION (Keeps 1 copy of Forms 1, 2, and 3)
Form 3 (2 copies)
1 copy Form 3
SAMPLE MANAGEMENT OFFICE
Form 3
QA MANAGER
Forms 1 and 2
DATA BASE
Forms 1 and 2

Figure 6.8. Eastern Lake Survey data flow scheme.

activities to be performed. Where possible, these simulations include helicopter sampling from a lake and sample preparation in a field station. If these opportunities are not available, sampling and field measurements are made from a boat, and the field station activities are simulated in a laboratory.

7.0 FIELD MEASUREMENT QUALITY CONTROL CHECKS

Field measurements are those made by the field crews at the lake sites and by the field laboratory personnel at the field laboratory. These measurements are described in Sections 7.1 and 7.2, respectively.

7.1 Lake Site Measurements

The lake site measurements consist of three Hydrolab determinations (lake-water temperature, pH, and specific conductance), Secchi disk transparency, air temperature, and site depth. All measurements are recorded on Form 1 - Lake Data.

7.1.1 Hydrolab - The Hydrolab instrument is used to measure lake-water temperature, pH, and specific conductance in situ.

The QC procedures consist of calibrating the instrument before and after each excursion and monitoring the drift between calibrations. These procedures are described in detail in Morris et al., 1986. The following is a summary of QC procedures for the Hydrolab.

Lake-water temperature - There is no calibration control for temperature. The instrument is calibrated at the factory and should be accurate to 0.2°C. The accuracy is checked each day against a National Bureau of Standards (NBS)-traceable thermometer and if an error of 1°C or more is found, the manufacturer should be consulted. An error of this size usually indicates a malfunction of the instrument.

pH - Following the daily calibration, a quality control check sample standard (QCCS) of CO_2-saturated deionized water is measured. The QCCS has a theoretical pH value of 3.91 at standard temperature and pressure. The instrument drift is determined by remeasuring the QCCS after completion of all sample analyses. If either QCCS reading deviates from the theoretical pH by more than ±0.1 pH unit, the data qualifier "N" is recorded on Form 1. The procedure for Hydrolab pH measurement is described in Morris et al., 1986.

Specific conductance - A procedure for the specific conductance determination is described in Morris et al., 1986. A KCl calibration standard of 147 µS/cm is used. The error allowed on the calibration standards is 1 percent of the highest reading on the scale (2,000 µS/cm) used. The allowed error on the QCCS (CO_2-saturated deionized water having a standard specific conductance value of 50 µS/cm) is ±20 µS/cm.

7.1.2 Secchi Disk Transparency - The Secchi disk transparency should be taken on the shady side of the helicopter, and the observer must not wear sunglasses.

7.1.3 Air Temperature, Site Depth, and Elevation - Air temperature is measured by one of the helicopter instruments. An electronic depth recorder mounted in the helicopter is used to locate the sampling site, which ideally should be the deepest part of the lake. Once daily the depth recorder is checked against a calibrated sounding line. The helicopter pilot must calibrate the altimeter periodically. Site elevation is checked by helicopter instrumentation to confirm the map reading; if a discrepancy occurs, it should be recorded on Form 1.

7.2 Field Laboratory Measurements

The field laboratory measurements consist of DIC, pH, turbidity, and true color. The data are recorded on Form 2. The QC procedures are described in detail in Morris et al., 1986. This section contains a summary of the QC procedures.

7.2.1 DIC - DIC is measured in routine, duplicate, and field audit samples using the Dohrman Model DC-80 carbon analyzer. The measurement procedure follows:

1. Initial calibration is performed using the working standard (10.00 mg/L C).
2. Two QC standards (2.00 mg/L C and 20.00 mg/L C) are measured to verify the initial calibration.
3. If both QC standards are within 10 percent of the theoretical concentration, the values are entered in the DIC logbook and analysis proceeds. If the standards are not within 10 percent, then steps 1 and 2 are repeated.
4. A calibration blank is measured.
5. If the calibration blank is less than 0.1 mg/L C, the value is recorded and sample analysis continues. If the calibration blank is 0.1 mg/L C or greater, then (1) the laboratory supervisor should be informed, (2) corrective action must be taken, and (3) steps 1 through 5 are repeated. Normally, one calibration blank is analyzed per batch.
6. DIC is measured for eight samples.

7. A 2.0 mg/L C QCCS is analyzed to check the calibration.

8. If the QCCS is within 10 percent of theoretical concentration, the value is recorded in the logbook and sample analysis proceeds. If the QCCS is not within 10 percent, it should be determined whether there is enough left of the samples associated with the unacceptable QCCS to reanalyze them. If enough sample is left, steps 1 through 7 are repeated, including analysis of all samples since the last acceptable QCCS. If not enough sample remains, the unacceptable QCCS value is recorded in the DIC logbook and the sample ID numbers associated with the unacceptable QCCS are noted. Sample analysis must not continue until acceptable QCCS values are obtained.

9. One sample is measured in duplicate per batch. These duplicates are called trailer duplicates. If the difference between the two measurements is greater than 10 percent, another sample is measured in duplicate. If the difference is still greater than 10 percent, the laboratory supervisor should be notified, and the problem should be noted on Form 2 with a data qualifier.

10. When sample analysis is complete, a final QC check is required, and the relevant QC information is recorded on Form 2, Batch QC Field Data.

7.2.2 pH - pH is determined in routine, duplicate, and field audit samples using the Orion Model 611 pH meter with Orion Ross epoxy body combination pH electrode. The measurement procedure is as follows:

1. The instrument is standardized according to the manufacturer's instructions.

2. The pH of the pH 4 and the pH 7 buffers is measured and the results are recorded in the logbook. If either differs from the certified value by more than 0.02 pH units, steps 1 and 2 are repeated. If acceptable results cannot be obtained, the electrode is replaced and the above procedure is repeated. (The old electrodes should be shipped to the QA manager at EMSL-LV where they will be tested further.)

3. When satisfactory results are obtained for the buffers, the pH of a pH 4.00 QC sample is measured and the result is recorded in the logbook. If the reading differs from 4.0 by more than ±0.1 pH unit, steps 1 and 2 are repeated, and the pH of a fresh QCCS is measured. If acceptable results are still not obtained, the laboratory manager should be consulted. Lake samples are not to be analyzed until an acceptable value for the QCCS has been obtained.

4. Samples are measured for pH. After every five samples, a pH 4.00 QC sample is measured and the result is recorded in the logbook. If the measured pH of the QC sample is 4.0 ± 0.1 pH units, measurement of samples proceeds.

5. If the QCCS is not acceptable, it should be determined whether there is a sufficient amount of sample remaining to repeat the analysis. If so, steps 1 through 3 are repeated and all samples analyzed since the last acceptable QCCS are reanalyzed. If not enough sample remains, the sample ID numbers associated with the unacceptable QCCS are recorded in the logbook. Steps 1 through 3 are repeated before proceeding with sample analysis.

6. One sample per batch is measured in duplicate. If the difference between the two measurements is greater than 0.1 pH unit, another sample is measured in duplicate. If the difference is still greater than 0.1 pH unit, the laboratory supervisor should be notified, and the problem should be noted on Form 2 with a data qualifier.

7. After the last sample in a batch has been analyzed, a final QCCS is analyzed and the value is recorded in the logbook.

8. When this analysis is completed, the relevant QC information is recorded on Form 2.

7.2.3 Turbidity - Turbidity is determined in routine, duplicate, and blank samples using the Monitek Model 21 laboratory nephelometer. The measurement procedure is as follows:

1. The nephelometer, set on range 2, is zeroed and then is calibrated on range 20 with a 10.0 NTU standard, following the manufacturer's recommendations.

2. Calibration linearity is verified by analyzing 1.7, 5.0, and 20.0 NTU QC samples. (The 20.0 NTU QC sample is measured on range 200.) The measured values must be 1.7 ± 0.3, 5.0 ± 0.5, and 20.0 ± 1.0. If the measured values are unacceptable, step 1 is repeated. Acceptable results must be obtained prior to sample analysis. Acceptable results for the 5.0 NTU QC sample are recorded on Form 2.

3. After every eight samples, a 5.0 NTU QC sample is measured. If the measured value is 5.0 ± 0.5 NTU, QC and sample results are recorded on Form 2.

4. If the QC measurement is unacceptable, the instrument must be recalibrated and the previous eight samples must be reanalyzed. Acceptable QC values are recorded on Form 2 along with associated sample results.

7.2.4 True Color - The only QC check on true color is that one sample per batch is measured in duplicate. If the two measurements differ by more than 10 percent, another sample is measured in duplicate. If acceptable results are still not obtained, the laboratory supervisor must be notified and a data qualifier must be recorded on Form 2 with the results. Acceptable results are also recorded on Form 2.

8.0 ANALYTICAL PROCEDURES

Table 8.1 lists the analytical procedures that are used to determine each parameter. A detailed description of these procedures is provided in the methods manual (Hillman et al., 1986). Internal QC checks on the analytical procedures are discussed in the next section.

TABLE 8.1. LIST OF PARAMETERS AND CORRESPONDING MEASUREMENT METHODS

Parameter	Method[a]
1. Acidity (BNC)	Titration with Gran plot
2. Alkalinity (ANC)	Titration with Gran plot
3. Aluminum, total	EPA Method 202.2 AAS (furnace)
4. Aluminum, total extractable	Extraction with 8-hydroxyquinoline into MIBK followed by AAS (furnace)
5. Ammonium, dissolved	EPA Method 350.1
6. Calcium, dissolved	EPA Method 215.1 - AAS (flame)
7 Chloride, dissolved	Ion chromatography
8. Fluoride, total	Ion selective electrode
9. Inorganic carbon, dissolved	Instrumental (Similar to DOC)
10. Iron, dissolved	EPA Method 236.1 - AAS (furnace)
11. Magnesium, dissolved	EPA Method 242.1 - AAS (flame)
12. Manganese, dissolved	EPA Method 243.1 - AAS (flame)
13. Nitrate, dissolved	Ion chromatography
14. Organic carbon, dissolved	EPA Method 415.2
15. pH	pH electrode and meter
16. Phosphorus, total	USGS Method I-4600-78 or Modified USGS Method
17. Potassium, dissolved	EPA Method 258.1 - AAS (flame)
18. Silica, dissolved	USGS Method I-2700-78
19. Sodium, dissolved	EPA Method 273.1 - AAS (flame)
20. Sulfate, dissolved	Ion chromatography
21. Specific conductance	EPA Method 120.1

[a] AAS methods are taken from U.S. EPA, 1983. Laboratories that have ICP instrumentation may use EPA Method 200.7, reproduced in Appendix A of Hillman et al., 1986, for determining Ca, Fe, Mg, and Mn, providing they can demonstrate the detection limits specified in Table 4.1. If the ICP instrumentation is not able to meet the required detection limits, it may still be used to analyze samples which contain the analytes at concentrations greater than 10 times the ICP detection limit. Other samples must be analyzed by furnace or flame AAS.

9.0 ANALYTICAL INTERNAL QUALITY CONTROL

9.1 Sample Receipt

All samples received by the analytical laboratory should be checked in by a receiving clerk who (1) records the date received on the shipping form, (2) checks the samples to identify discrepancies with the shipping form, (3) fills out the "sample condition" portion of the shipping form, and (4) mails a copy of the completed shipping form to the Sample Management Office (SMO). The "sample condition" column should note such information as leakage in shipping, insufficient sample, noticeable suspended particulates, partially frozen samples, and the temperature of the sample containers. If there are any discrepancies, the field base coordinator must be notified immediately. These data are kept on a computer file by SMO and are available to interested parties. The laboratory retains a copy of the completed shipping form for the laboratory records. The samples are refrigerated as soon as possible.

Samples are received already preserved and ready for analysis. Sample aliquots 2, 3, 4, 5, and 6 must be kept refrigerated and in the dark while not in use. When an analysis is to be performed, the analyst should remove an aliquot from the sample and return the sample to the refrigerator as soon as possible.

Even after all analyses have been completed and the results have been checked, samples should remain stored in a refrigerator at 4°C, in case reanalysis is necessary.

9.2 Sample Analysis

Procedures given in the methods manual (Hillman et al., 1986) are to be followed exactly for each parameter whose value must be measured. Table 8.1 is a list of all required parameter measurements and the associated methods. Table 4.1 lists the required precision, expected ranges, and detection limits for each parameter. All analyses for each parameter must be performed within the specified holding times given in Table 9.1.

9.3 Analytical Laboratory Documentation for Quality Control

The following documents and information must be updated constantly and must be available to the analyst and the supervisor involved in the project:

- laboratory standard operational procedures (SOP's) - detailed instructions about the laboratory and instrument operations.

TABLE 9.1. LIST OF MAXIMUM HOLDING TIMES

Holding Time	7 days	14 days	28 days	28 days[a]
Parameter	NO_3^-[b]	Alkalinity (ANC)	Total P	Ca
	pH[c]	Acidity (BNC)	NH_4^+	Mg
	Total extractable Al	Specific Conductance	Cl^-	K
		DIC	SO_4^{2-}	Na
		DOC	F^-	Total Al
			SiO_2	Mn
				Fe

[a] Although the EPA (U.S. EPA, 1983) recommends a maximum holding time of 6 months for these metals, this study requires that all of the metals be determined within 28 days. This is to ensure that significant changes do not occur and to obtain data in a timely manner.

[b] Although the EPA (U.S. EPA, 1983) recommends that nitrate in unpreserved samples (un-acidified) be determined within 48 hours of collection, evidence exists (Peden, 1981 and APHA et al., 1985) that nitrate is stable for 2 to 4 weeks if stored in the dark at 4°C.

[c] Although the EPA (U.S. EPA, 1983) recommends that pH be measured immediately after sample collection, evidence exists (McQuaker et al., 1983) that it is stable for up to 15 days if stored at 4°C and sealed from the atmosphere. Seven days is specified here for added precautions. The pH is also measured in a sealed sample at the field station within 12 hours of sample collection.

- laboratory QA plan - clearly defined laboratory protocol, including personnel responsibilities and use of QC samples.

- list of in-house samples - including projected dates for completion of analyses; allows analyst to schedule further analyses.

- instrument performance study information - information on baseline noise, calibration standard response, precision as a function of concentration, and detection limits; used by analyst and supervisor to evaluate daily instrument performance.

- QC charts - the most recent QC charts with 99 percent and 95 percent control limits for all QCCS and detection limit QCCS, generated and updated for each batch. The same QCCS must be used for all QC charts to ensure the continuity of the charts. (Note: The purpose of preparing QCCS charts is to ensure that the actual control limits do not exceed the limits given in Table 9.2.)

- data sheet QC report - report by the laboratory manager reviewing QC results for each parameter and flagging all results outside statistically established QC limits for reanalysis before data are submitted to recipients.

9.4 Internal Quality Control Within Each Method

Internal QC must be an integral part of any measurement procedure to ensure that results are reliable. A summary of internal QC procedures for each method is given in Table 9.3. QC procedures for certain measurements (pH, BNC, ANC, and specific conductance) are detailed in the appropriate method description in Hillman et al., 1986. Details on internal QC procedures for automated colorimetric analyses (total P, ammonium, and silica), instrumental carbon analyses (dissolved organic carbon and dissolved inorganic carbon), ion chromatography analyses (nitrate, chloride, fluoride, and sulfate), and atomic absorption or emission analyses (Ca, Mg, K, Na, Mn, Fe, total Al, and total extractable Al) are described below.

1. Initial Calibration - An initial calibration is performed as required for each analytical method. Next, the linear dynamic range (LDR) is determined for the initial calibration. The concentrations of the calibration standards must bracket the expected sample concentrations. (Occasionally the standards suggested by a method must be adjusted to meet this requirement.) The low standard should not be greater than 10 times the detection limit. If during the analysis the concentration of a sample is above the LDR, two options are available. One option is to dilute and reanalyze the sample. In this case, the diluent should have a matrix similar to the sample matrix with respect

TABLE 9.2. MAXIMUM CONTROL LIMITS FOR QUALITY CONTROL CHECK SAMPLES (QCCS)

Parameter	Maximum Control Limit for QCCS (% Difference from Theoretical Concentration of QCCS)
Al, total extractable	±20%
Al, total	±20%
Ca	±5%
Cl^-	±5%
DIC	±10%
DOC	±10%
F^-, total	±5%
Fe	±10%
K	±5%
Mg	±5%
Mn	±10%
Na	±5%
NH_4^+	±10%
NO_3^-	±10%
P, total	±20%
SiO_2	±5%
SO_4^{2-}	±5%
Specific Conductance	±2%

TABLE 9.3. SUMMARY OF INTERNAL QUALITY CONTROL CHECKS FOR ANALYSIS METHODS

Parameter or Method	QC Check	Control Limits	Corrective Action[a]
ANC, BNC, pH	1. Titrant standardization crosscheck	1. Relative differences <5%	1. Restandardize titrants.
	2. Electrode calibration (Nernstian response check)	2. Slope = 1.00 ± 0.05	2. Recalibrate or replace electrode.
	3. pH QCCS (pH 4 and 10) analysis	3. pH 4 = 4.00 ± 0.05 pH 10 = 10.00 ± 0.05	3. Recalibrate electrode.
	4. Blank analysis (salt spike)	4. |Blank| ≤10 µeq/L	4. Prepare fresh KCl spike solution.
	5. Duplicate analysis	5. RSD ≤10% (ANC and BNC) ± 0.05 pH units (pH)	5. Refine analytical technique, analyze another duplicate.
	6. Protolyte comparison	6. See Hillman et al., 1986	6. See Hillman et al., 1986.
Ions (Cl^-, Total F^-, NH_4^+, NO_3^-, SO_4^{2-}) Metals (Total Al, total extractable Al, Ca, Fe, K, Mg, Mn, Na) SiO_2, Total P, DIC, DOC, Spec. Cond.	1a. Initial QCCS analysis (calibration and verification)	1a,b. The lesser of the 99% CI or value given in Table 9.2	1a. Prepare new standards and recalibrate.
	1b. Continuing QCCS analysis (every 10 samples)		1b. Recalibrate. Reanalyze associated samples.
	2a. Detection limit determination (weekly)	2a. Detection limits given in Table 4.1	2a,b. Optimize instrumentation and technique.
	2b. DL QCCS analysis (daily; metals and total P only)	2b. % Recovery = 100 ± 20%	
	3. Blank analysis	3a. Blank ≤2 x DL (except sp. cond.)	3a,b. Determine and eliminate contamination source. Prepare fresh blank solution. Reanalyze associated samples.
		3b. Blank ≤0.9 µS/cm (sp. cond. only)	
	4. Duplicate analysis	4. Duplicate precision (%RSD) limits given in Table 4.1	4. Investigate and eliminate source of imprecision. Analyze another duplicate.

(continued)

---

[a] To be followed when QC check is outside control limits.

TABLE 9.3. (Continued)

Parameter or Method	QC Check	Control Limits	Corrective Action[a]
Ions (Cl^-, Total F^-, NH_4^+, NO_3^-, SO_4^{2-}) Metals (Total Al, total extractable Al, Ca, Fe, K, Mg, Mn, Na) SiO_2, Total P, DIC, DOC, Spec. Cond.	5. Matrix spike (except ext. Al, DIC, and spec. cond.)	5. % Recovery = 100 ± 15%	5. Analyze 2 additional spikes If one or both outside control limits, analyze all samples in that batch by method of standard additions.
	6. Resolution test (IC only)	6. Resolution $\geq$60%	6. Clean or replace separator column. Recalibrate.

[a] To be followed when QC check is outside control limits.

to all preservatives (acid type and concentration) used. Alternatively, two concentration ranges may be calibrated. Samples are first analyzed on the lower concentration range. Each sample whose concentration exceeds the upper end of the LDR is then reanalyzed on the higher concentration range. If this option is taken, separate QC samples must be analyzed and reported for each range.

2. QCCS - Immediately after standardization of the instruments, a QCCS containing the analyte of interest at a concentration in the mid-calibration range must be analyzed. QCCS may be obtained commercially or may be prepared by the analyst from a source which is independent from the calibration standards. The calibration QC sample must be analyzed to verify the calibration curve prior to any sample analysis, after every 10 samples, and after the last sample. The observed value for the QC sample must not differ from the theoretical value by more than the limits given in Table 9.2. When an unacceptable value for the calibration QC sample is obtained, the instrument must be recalibrated and all samples that were analyzed after the last acceptable QC sample must be reanalyzed. Furthermore, the observed concentrations for the QC sample must be plotted on a QC chart and 99 percent and 95 percent confidence intervals must be developed. To ensure the continuity of QC charts, a QCCS sample of the same theoretical concentration must be used throughout the plotting process. The 99 percent control limit must not differ from the theoretical concentration by more than the limits given in Table 9.2. If it does, the QA manager must be consulted. After each day of analysis, QC charts should be updated, cumulative means should be calculated, and new warning and control limits (95 percent and 99 percent, respectively) should be determined. To indicate bias for a given analysis, there must be at least seven successive points on one side of the theoretical mean. If bias is indicated, analysis must be stopped and an explanation must be sought. Current control charts must be available to the analyst and available during on-site evaluations.

3. Detection Limit QCCS - This is a low-level QC sample containing the analyte of interest at a concentration two to three times the required detection limit. This QC sample must be analyzed once per batch for the parameters total extractable Al, total Al, dissolved metals (Ca, Fe, K, Mg, Mn, Na), and total P. The results are reported on Form 20, Blanks and QCCS Results. (See Table 9.4.) The purpose of the detection limit QC sample is to eliminate the necessity of formally determining the detection limit on a daily basis. The measured value must be within 20 percent of the theoretical concentration. If it is not, the problem must be identified and corrected, and an acceptable result must be obtained prior to sample analysis.

TABLE 9.4. LIST OF DATA FORMS USED BY THE ANALYTICAL LABORATORY[a]

Data Form	Description
11	Summary of Sample Results
13	Alkalinity and Acidity Analyses Results
14[b]	QC Data for Alkalinity and Acidity Analyses
15[b]	Specific Conductance (Measured and Calculated)
16[b]	Anion-Cation Balance Calculations
17	Ion Chromatography Resolution Test
18	Detection Limits
19	Sample Holding Time Summary
20	Blanks and QCCS Results
21	Matrix Spikes Results
22	Duplicates Results
23	Standard Additions Results

[a] These forms are shown in Appendix A.

[b] Form not required to be submitted with data package but recommended for internal QC requirements.

4. Calibration Blank - A calibration blank must be analyzed once per batch, immediately after the initial calibration, to check for baseline drift. Rezero if necessary. The calibration blank is defined as a "0" mg/L standard and contains only the matrix of the calibration standards. The observed concentration of the calibration blank must be less than or equal to twice the required detection limit. If it is not, the instrument must be rezeroed and the calibration must be rechecked.

5. Reagent Blank - A reagent blank must be prepared and analyzed for each batch of samples for methods which require sample preparation (dissolved SiO_2 and total Al). A reagent blank is defined as a sample composed of all the reagents (in the same quantities) used in preparing a real sample for analysis. It is also carried through the same digestion/extraction procedure as a real sample. The concentration of the reagent blank must be less than or equal to twice the required detection limit. If the concentration exceeds this limit, the source of contamination must be investigated and eliminated. A new reagent blank must then be prepared and analyzed for any sample in which the high reagent blank value contributed significantly (>10 percent) to the value of the parameter in question. If a high reagent blank problem cannot be corrected, then the QA manager must be contacted. Reagent blank results are reported on Form 20 but are not subtracted from sample results.

6. Preliminary Sample Analysis - Approximately seven samples and a reagent blank must be analyzed prior to matrix spike and duplicate analyses to determine approximate endogenous sample concentrations.

7. Matrix Spike Analysis - One matrix spike must be prepared for each batch. It is prepared by spiking an aliquot of a sample* with a known quantity of analyte prior to analysis. The spike concentration must be twice the endogenous level or ten times the required detection limit, whichever is larger. Also, the volume of the spike added must be negligible (less than or equal to one percent of the sample aliquot volume). The spike recovery must be 100 ± 15 percent to be acceptable. If the recovery is not acceptable for all parameters, two additional, different samples must be spiked with the analyte in question, must then be analyzed, and recoveries must be calculated. If one or both recoveries are not 100 ± 15 percent, the entire batch must be analyzed by standard additions for the parameter in question. The standard

---

*QA analysis on a full sample is recommended. If sufficient sample volume is not available, QA analysis may be performed on a per-aliquot basis.

addition is performed by analyzing the sample, the sample plus a spike at about the endogenous level, and the sample plus a spike at about twice the endogenous level. The concentration of the matrix spike must not exceed the linear range of the method. For this reason, the matrix spike for furnace analyses, which determine low levels of analyte, must be chosen judiciously and may be different than suggested above. The samples may be diluted or the spike levels may be adjusted so that the linear range is not exceeded when performing standard additions for furnace AA analyses. A matrix spike is not required for total extractable Al analyses. The percent recovery of spikes is calculated as described below:

$$\%\ \text{spike recovery} = \frac{\begin{matrix}\text{value of sample}\\ \text{plus spike}\end{matrix} - \begin{matrix}\text{value of unspiked}\\ \text{sample}\end{matrix}}{\text{value of spike added}} \times 100$$

8. Duplicate Sample Analysis - One sample per batch must be prepared and analyzed in duplicate for each parameter. The relative standard deviation is plotted on a QC chart and 99 percent and 95 percent confidence intervals are established. Initial control limits are set at the precision levels given in Table 4.1. The control limits should not exceed these values. If they do, the QA manager must be notified immediately. If duplicate values fall outside the control limits, an explanation must be sought (such as instrument malfunction, calibration drift, etc.). A second, different sample must then be analyzed in duplicate. No further samples may be analyzed until duplicate sample results are within the control limits, unless approval is given from the QA manager. The percent relative standard deviation (%RSD) is calculated as described below:

$$\%\text{RSD} = \frac{s}{\overline{X}} \times 100$$

$$s = \left(\frac{\Sigma(\overline{X} - X)^2}{n - 1}\right)^{1/2}$$

where: s is the standard deviation

X is a datum

$\overline{X}$ is the mean

n is the population

6 3

9. Ion Chromatography Resolution Test - An ion chromatography resolution test must be performed once per analytical run (day) by analyzing a standard containing approximately equal concentrations of SO_4^{2-} and NO_3^- (~1 mg/L). If the resolution does not exceed 60 percent, the column should be replaced and the resolution test should be repeated.

10. Continuing Sample Analysis - The remaining samples are analyzed if the reagent blank, matrix spike, duplicate, and QC samples are within limits. After every 10 (or fewer) samples and after the last sample, a QC sample must be analyzed to continually verify the calibration curve. If the measured value differs from the theoretical value by more than the limits given in Table 9.2, the instrument is recalibrated and the previous 10 samples are reanalyzed.

9.5 Overall Internal Quality Control

Once the value of each parameter in a sample is determined, there are several procedures for checking the correctness of analyses. These procedures are outlined in the following subsections.

9.5.1 Anion-Cation Balance - Theoretically, the acid neutralizing capacity (ANC) of a sample equals the difference, expressed as microequivalents per liter (µeq/L), between the concentration of cations and the concentration of anions in a sample (Kramer, 1982). In practice, this is rarely the case; deviations are caused by analytical variability and the presence of ions (protolytes) that are not measured (e.g., organic ions). The concentrations of these unmeasured ions can be significant in natural lake samples. The percent ion difference (%ID) calculation below utilizes the ANC value to take these ions into account; as a result, the calculation is more accurate. For each sample, the percent ion difference is calculated as follows:

$$\%ID = \frac{ANC + \Sigma \text{ anions} - \Sigma \text{ cations}}{TI} \times 100$$

where:

Σ anions = $[Cl^-] + [F^-] + [NO_3^-] + [SO_4^{2-}]$

Σ cations = $[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] + [NH_4^+]$

TI = total ion strength = ANC + Σ anions + Σ cations + $2[H^+]$

ANC $\approx$ Alkalinity

$[H^+] = (10^{-pH}) \times 10^6$ µeq/L

64

JW-61-85 [illegible]
4-10-85 [illegible]

TABLE 9.5. CHEMICAL REANALYSIS CRITERIA

A. Anion-Cation Balance

Total Ion Strength (μeq/L)	% Ion Maximum Balance Difference[a]
<50	60
≥50 <100	30
≥100	15

B. Specific Conductance

Measured Specific Conductance (μS/cm)	Maximum % Specific Conductance Difference[a]
<5	50
≥5 <30	30
≥30	20

---

[a] If the absolute value of the percent difference exceeds these values, the sample is reanalyzed. When reanalysis is indicated, the data for each parameter is examined for possible analytical error. Suspect results are then redetermined and the above percent differences are recalculated (Peden, 1981). If the percent differences for reanalyzed samples are still unacceptable, or no suspect data are identified, the QA manager must be contacted for guidance.

All concentrations are expressed as microequivalents per liter. A list of factors for converting mg/L to µeq/L for each parameter is given in the methods manual (Hillman et al., 1986). Samples which have a poor ion balance are reanalyzed. Table 9.5 lists the criteria for reanalysis. Prior to reanalysis, the data should be checked for possible causes of poor ion balance. This check may indicate which analytical results give rise to poor ion balance and hence, the parameters for which the sample should be reanalyzed. Also, careful examination of the data may explain the poor ion balance. For example, if the percent ion difference is negative and the DOC >3 mg/L, unmeasured organic anions are most likely responsible; thus, reanalysis is unnecessary. The QA manager must be contacted when questions arise regarding reanalysis.

9.5.2 Conductance Balance - An approximation of the conductance of a sample can be calculated by adding together the equivalent conductances for each measured ion at infinite dilution. The calculated conductances are determined by multiplying the concentration of each ion by the appropriate factor given in Table 9.6. The percent conductance difference (%CD) is calculated as follows:

$$\%\ CD = \frac{\text{calculated cond. - measured cond.}}{\text{measured conductance}} \times 100$$

Samples which have %CD's exceeding the limits listed in Table 9.5 are reanalyzed. As with the percent ion difference calculation, an unacceptable value for %CD indicates either the presence of unmeasured ions or an analytical error in the measurement. For the surface waters sampled, the ions included in the %CD calculation are expected to account for 90 to 100 percent of the ions in a sample. However, in contrast to the percent ion difference calculation, there is no term in the %CD calculation to account for protolytes that are not specifically determined. The QA manager must be contacted when questions arise regarding reanalysis.

9.6 Instrumental Detection Limits

Instrumental Detection Limits (IDL's) must be determined and reported weekly for each parameter except pH, specific conductance, ANC, and BNC. For this study, the detection limit is defined as three times the standard deviation of 10 nonconsecutive replicate reagent or calibration blank analyses. Calibration blanks are analyzed when a method does not require a reagent blank. In some analyses, such as those using ion chromatography and Technicon AutoAnalyzers, a signal may or may not be obtained for a blank analysis. If a signal is not obtained for a blank analysis, the

66

TABLE 9.6. CONDUCTANCE FACTORS OF IONS[a]

Ion	Specific Conductance (µS/cm at 25°C) per mg/L	Ion	Specific Conductance (µS/cm at 25°C) per mg/L
Ca^{2+}	2.60	Na^+	2.13
Cl^-	2.14	NH_4^+	4.13
CO_3^{2-}	2.82	SO_4^{2-}	1.54
H^+	3.5×10^5 (per mole/L)	NO_3^-	1.15
HCO_3^-	0.715	K^+	1.84
Mg^{2+}	3.82	OH^-	1.92×10^5 (per mole/L)

$[H^+]$ moles/L = 10^{-pH}

pH = initial pH measured before acidity titration.

$$[OH^-] = \frac{Kw}{[H^+]}$$

$$HCO_3^- = \frac{5.080\ [DIC(mg/L)]\ [H^+]\ K_1}{[H^+]^2 + [H^+]\ K_1 + K_1K_2}$$

$$CO_3^{2-} = \frac{4.996\ [DIC(mg/L)]\ K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$

$$K_1 = 4.4463 \times 10^{-7} \quad K_2 = 4.6881 \times 10^{-11}$$

---

[a] Taken from American Public Health Association et al., 1985, and from Weast, 1972.

instrumental detection limit is defined as three times the standard deviation of 10 nonconsecutive replicate analyses of a standard whose concentration is three to four times the required detection limit. Detection limits must not exceed the limits listed in Table 4.1.

9.7 Data Reporting

Results from each method are recorded on the appropriate data forms (Table 9.4). After a sample (aliquots 1 through 7) is completely analyzed, the results are summarized on the Data Form 11 and are reported to the number of decimal places listed in Table 9.7. Results are annotated by the data qualifiers (tags) listed in Table 9.8, where applicable. After a form is completed, the analytical laboratory supervisor must sign it, indicating he has reviewed the data and that the samples were analyzed exactly as described in the methods manual (Hillman et al., 1986). All deviations from the manual require the authorization of the QA manager prior to sample analysis.

Copies of raw data must be submitted as requested by the QA manager. All original raw data must be retained by the lab until notified otherwise by QA manager. Raw data include data system printouts, chromatograms, notebooks, QC charts, standard preparation data, and all information pertinent to sample analysis.

9.8 Daily Evaluation of Quality Control Data

Each laboratory should make a Daily Sample Status Report by telephone to the QA manager (or his authorized representative) as directed. The objective of these reports is to keep the QA manager informed of the status of the internal and external QC checks in the laboratory in order to identify and solve problems that may arise. The reports also allow the QA manager to obtain preliminary results for the blanks, duplicates, and laboratory and field audit samples that are double-blind to the laboratories. (A discussion of blind and double-blind samples is presented in Section 10.) Otherwise, these data would not be available for QA/QC data evaluation until they were reported by the laboratories, which may be up to 35 days after the samples are received. During the daily telephone contact, the QA manager (or designee) completes the Telephone Record Log shown in Appendix B.

After each day of analysis, QC charts are updated and new control and warning limits are determined. The QA chemist then performs a QC audit in which all the data are reviewed. Any values that lie outside the control or warning limits are checked to verify that they are not the result of a transcription error. If bias is indicated (seven successive points on one side of the cumulative mean), analyses are stopped and an explanation is sought. Copies of the plots are given to the analytical laboratory supervisor, the QA chemist, and each analyst.

TABLE 9.7. LIST OF DECIMAL PLACE REPORTING REQUIREMENTS

Parameter	Recommended Number of Decimal Places in Reported Results[a]
Al, total extractable	3
Al, total	3
Acidity (BNC)	1
Alkalinity (ANC)	1
Ca	2
Cl^-	2
DIC	2
DOC	1
F^-, total	3
Fe	2
K	2
Mg	2
Mn	2
Na	2
NH_4^+	2
NO_3^-	3
pH	2
P, total	3
SiO_2	2
SO_4^{2-}	2
Specific Conductance	1

---

[a] Report to the number of decimal places in the actual instrument detection limit (IDL). Where applicable, no more than three significant figures should be reported.

TABLE 9.8. NATIONAL SURFACE WATER SURVEY LAB/FIELD DATA QUALIFIERS (TAGS)

Qualifier	Indicates
A	Instrument unstable
B	Redone, first reading not acceptable
C	Instruments, sampling gear not vertical in water column
D	Slow stabilization
E	Hydrolab cable too short
F	Result outside QA criteria (with consent of QA manager)
G	Result obtained from method of standard additions
H	Holding time exceeded criteria (Form 19 only)
J	Result not available; insufficient sample volume shipped to laboratory from the field
K	Result not available; entire aliquot not shipped
L	Not analyzed due to interference
M	Result not available; sample lost or destroyed by lab
N	Not required
P	Result outside QA criteria, but insufficient volume for reanalysis
Q	Result outside QA criteria
R	Result from reanalysis
S	Contamination suspected
T	Leaking container
U	Result not required by procedure; unnecessary
V	Anion-cation balance outside criteria due to high DOC
W	% Difference (%D) calculation (Form 14) outside criteria due to high DOC
X	Available for miscellaneous comments in the field only
Y	Available for miscellaneous comments in the field only
Z	Available for miscellaneous comments in the field only
<	Measurements taken at <1.5 m

10.0 PERFORMANCE AND SYSTEM AUDITS

10.1 Performance Audit Samples

Field and laboratory audit samples are used as part of the QA activities of the ELS-I. The audit samples are shipped to the analytical laboratories from the field stations as though they were routine lake samples. Every attempt is made to assure that the analytical laboratory does not recognize the audit samples as different from the routine lake samples. As a result, the audit samples are double blind to the analytical laboratory. That is, the laboratory neither recognizes them as audit samples nor knows their compositions.

10.1.1 Field Audit Samples - The purpose of field audit samples is to identify problems affecting data quality that may occur during sample processing, shipment, or analysis. These problems could include sample contamination, sample degradation, solvent evaporation, and improper or inaccurate sample analysis. When used in conjunction with laboratory audit samples, the analysis of these samples provides data that can be used to distinguish field station problems from analytical laboratory problems. There are two types of field audit samples: synthetic field audit samples and natural field audit samples.

The synthetic field audit samples are prepared at a central laboratory and are sent to the field laboratory to be processed through all the filtration and preservation steps and labeled as though they were authentic lake samples. Thus, they are single-blind samples to the field laboratory (i.e., recognized as audit samples but of unknown composition) and, concurrently, double-blind samples to the analytical laboratory.

The desired composition of the synthetic field audit samples is shown in Table 10.1. Two formulations of synthetic samples are used for the ELS-I to test the sampling and analysis systems at both high and low concentrations of analytes.

Waters collected from Big Moose Lake in the Adirondack Mountains and from Lake Superior at Duluth, Minnesota, are utilized as natural audit samples for the survey. The waters of Big Moose Lake are low in alkalinity and thus are susceptible to acidic deposition; the Lake Superior waters represent a buffered system. These natural samples are passed through a 0.45μ filter and are maintained at 4°C to minimize changes in composition. Aliquots (2 L) are included as part of a batch.

10.1.2 Laboratory Audit Samples - The purpose of these samples is to identify problems affecting data quality that may occur during the analytical process. Thus, lab audit samples help verify the accuracy of analytical

TABLE 10.1. DESIRED COMPOSITION OF SYNTHETIC FIELD AND LABORATORY AUDIT SAMPLES FOR THE EASTERN LAKE SURVEY

Parameter	Low Concentration	High Concentration	Units
Acidity (BNC)*	10-50	100-200	µeq/L
Al (total and total extractable)	0.01-0.10	0.2-1.0	mg/L
Alkalinity (ANC)*	10-50	100-200	µeq/L
Ca	0.1-1	1-10	mg/L
Cl^-	0.1-1	1-5	mg/L
DIC	0.1-1.0	3-10	mg/L
DOC	0.1-1.0	10-20	mg/L
F^-, total	0.01-0.05	0.05-0.2	mg/L
Fe	0.02-1.0	1-10	mg/L
K	0.1-1	1-5	mg/L
Mg	0.1-1	1-5	mg/L
Mn	0.02-1.0	1-10	mg/L
Na	0.5-3	5-12	mg/L
NH_4^+	0.01-0.50	0.5-2.0	mg/L
NO_3^-	0.01-0.50	0.5-2.0	mg/L
P, total	0.005-0.03	0.01-0.1	mg/L

(continued)

---

*These parameters are related and affect the analytical results of one another.

Note: mass balance (anions vs. cations) must be maintained. Nitrogen/phosphorus ratio must be reasonable (10/20).

TABLE 10.1. (Continued)

Parameter	Low Concentration	High Concentration	Units
pH*	4-5	7-8	pH
SiO_2	1-5	10-20	mg/L
SO_4^{2-}	1-5	10-20	mg/L
Specific Conductance**	1-50	100-200	µS/cm

*These parameters are related and affect the analytical results of one another.
**To be determined by concentration of other parameters.
Note: Mass balance (anions vs. cations) must be maintained. Nitrogen/phosphorus ratio must be reasonable (10/20).

procedures and assure that the laboratory is maintaining the capability to properly analyze the samples.

The synthetic laboratory audit samples are sent to the field station from a central laboratory, already split into seven aliquots. The audit samples are labeled by the field laboratory personnel, are included in a batch with routine lake samples processed on the same day, and are shipped to the analytical laboratory for analysis.

The desired composition of the synthetic laboratory audit samples is given in Table 10.1. Two formulations of synthetic samples are used to test the analytical system at both high and low concentrations of analytes for the ELS-I.

10.1.3 Application of Audit Sample Data - Data are obtained from the analyses of the audit samples for the following purposes:

- to judge the performance of the field stations in the processing and shipment of samples
- to judge the continued capability of the analytical laboratories to properly analyze the samples

- to establish a statistically valid estimate of the overall bias and precision of the analyses
- to establish a statistically valid estimate of the stability of a typical lake sample when stored at 4°C by evaluating the natural lake sample over the period of the study.

Acceptance windows are established for the measurement of each parameter in the audit samples. The size of the windows is based upon the information available for each analytical method at the time the study is initiated. If the analytical results for a measurement fall outside the acceptance window, the EMSL-LV QA staff reviews the data to determine the cause of the problem and immediately contacts the analytical laboratory or field station, whichever is appropriate, to seek corrective action. Data for routine samples analyzed with the audit samples are also checked to determine if they were also affected by the problem. If they were affected, reanalysis of the samples in question is requested. The establishment of the acceptance windows is described in Section 11.

Approximately 150 synthetic audit samples and 60 natural-water audit samples are scheduled to be processed during the ELS-I. A statistical evaluation of the audit data should provide a good estimate of the bias and precision of the analytical methods for each required measurement. Furthermore, any changes over time in analytical results for the natural-water audit samples without corresponding change in the other audit samples can be attributed to lack of analyte stability. The findings of a comparative study between audit sample types will provide a statistically valid estimate of the true maximum holding times allowable for each type of analysis.

The audit samples are a key factor in the QA program for the ELS-I. It is intended that every effort be made to provide high-quality audit samples.

10.2 Quality Assurance System Audits (On-Site Evaluations)

The systems audit consists of qualitative evaluation of field and analytical laboratory facilities, equipment, and operations such as record keeping, data reporting, and QC procedures.

10.2.1 Field Operations On-Site Evaluation - Each field station and sampling team in the ELS-I can expect at least one on-site evaluation during the course of the sampling effort. This is an on-site inspection to review the sampling procedures, field station operations, and QA efforts.

For each field station and the corresponding sampling teams, the on-site evaluation should be conducted as soon as possible after the start of operations. The questionnaire given in Appendix C is used to assist in the evaluation.

The field auditor conducts an in-depth review of all field operations. This includes but is not limited to (a) interviewing the field base coordinator and the field laboratory supervisor, (b) observing the field station operations, (c) interviewing each sampling team, (d) accompanying one or more of the sampling teams during a sample excursion, and (e) writing a summary report that includes results, observations, and recommendations. If there are any problems, the evaluator must either attempt to correct them or must bring them to the attention of the field base coordinator.

10.2.2 Analytical Laboratory On-Site Evaluation - Each analytical laboratory participating in the ELS-I can expect a minimum of two in-depth on-site evaluations conducted by the EPA QA manager or his authorized representative. The questionnaire in Appendix D is used to assist in the on-site laboratory evaluation.

The first on-site laboratory evaluation is performed after the laboratory has successfully analyzed a set of Pre-Award Performance Evaluation (PE) samples for the contract-required parameters and before the actual survey analytical work begins. The PE samples contain up to the maximum number of analytes for which determination is required, in the expected concentration ranges. The PE sample results are scored using the ELS-I Pre-Award Score Sheet given in Appendix E. Grading emphasizes analytical accuracy, but a substantial portion of the grade depends on meeting the QA, internal QC, reporting, and deliverable requirements.

The auditor summarizes all observations in an On-Site Laboratory Evaluation Report and brings all problems that occur to the attention of the laboratory manager for corrective action.

The second on-site laboratory evaluation is conducted after approximately one-third of the ELS-I analyses have been completed. During the second on-site evaluation, QA sample (audit, duplicate, and blank) data and QC data received to date are reviewed. The laboratory questionnaire is updated, if necessary, noting all changes since the first on-site evaluation. An On-Site Laboratory Evaluation Report is written for this and for each additional on-site laboratory evaluation.

11.0 ACCEPTANCE CRITERIA

11.1 Audit Sample Results

Acceptance windows for single values from audit samples are based on previous interlaboratory analyses of the same sample material. The objective of creating windows is to predict intervals for acceptable single future values based on a sample mean ($\overline{x}$) and sample standard deviation (s) computed from n previously observed values. The limits of the windows are determined by using a t-statistic (t).

$$t = \frac{Z}{\sqrt{\frac{\mu}{r}}} \text{ is a Student's t}$$

where:

Z is the standard normal variate, having a normal distribution with a mean of 0 and a variance of 1

μ is a variable with a chi-square distribution with r degrees of freedom, and Z and μ are independent

The observed values X_1, X_2, X_3,.....X_n are independent and have a normal distribution ($\sim$N) with a population mean (μ) and variance(σ^2). A (1 - α) prediction interval for a single future value y is needed. Let $\bar{x}$ = sample mean and s = sample standard deviation. It is known that

$$y \sim N(\mu, \sigma^2) \text{ and } \overline{x} \sim N\left(\mu, \frac{\sigma^2}{n}\right).$$

Therefore,

$$y - \overline{x} \sim N\left(0, \sigma^2\left(1 + \frac{1}{n}\right)\right).$$

$$Z = \frac{y - \overline{x}}{\sigma\sqrt{1 + \frac{1}{n}}} \sim N(0, 1)$$

$$\mu = n-1\left(\frac{s^2}{\sigma 2}\right) \sim \chi^2_{(n-1)} \quad \text{and}$$

$$r = n-1.$$

Substituting,

$$t = \frac{\dfrac{y - \overline{x}}{\sigma\sqrt{1 + \frac{1}{n}}}}{\sqrt{\dfrac{(n-1)s^2}{(n-1)\ {}^2}}} = \frac{y - \overline{x}}{s\sqrt{1 + \frac{1}{n}}}.$$

The upper and lower limits of the window can be formalized as follows:

$$\overline{x} + (t)(s)\sqrt{1 + \frac{1}{n}} = \text{upper limit of the window}$$

$$\overline{x} - (t)(s)\sqrt{1 + \frac{1}{n}} = \text{lower limit of the window}$$

The Student's t-value (t) has n-1 degrees of freedom. The t-value is for a 2-tailed test with a cumulative probability of 0.975 (i.e., 2.5% probability on either side).

For predicting future values, wider windows than the standard 95% confidence interval about the mean are desirable. As the number of observed values increases, more variance occurs due to chance alone.

Initially, there may not be sufficient data ($n < 10$) available to provide good interval estimates. Arbitrary criteria may be used until 10 or more values are available. The windows should be periodically updated as more data are accumulated.

Grubbs' test (Grubbs, 1969) is applied to the data before interval estimation to detect outliers. The outliers are excluded from the computation of the windows.

Windows for matrix spike analysis results are computationally identical to those for audit sample results.

11.2 Duplicate Analysis Results

Acceptance criteria for the RSD are based on the upper 95th percentile of observed values of RSD. Because the RSD is affected by concentration, these criteria are applied only when the mean of the duplicate analyses exceeds the contract-required detection limit (CRDL) by a factor of 10.

Arbitrary acceptance criteria may be used until sufficient (at least 10) RSD values have been observed.

The distribution of the RSD values cannot be estimated accurately until sufficient RSD values have been observed. It is recommended that no outlier test be applied until the distribution has been estimated.

11.3 Corrective Action

Laboratories which fail to meet the acceptance criteria for analysis of audit samples, matrix spikes, or duplicates are required to repeat the analysis that produced the erroneous results. If results from the second analysis are still unacceptable, further corrective action must be initiated.

12.0 DATA MANAGEMENT SYSTEM

The purpose of the data base management system is to assemble and store data generated as part of the ELS-I, to provide basic reports of the survey results, to perform simple statistical analyses, and to provide data security. A detailed description of the system is given in the Data Management Proposal (ORNL, 1984). The relationship of data base management to the overall ELS-I is shown in Figure 12.1.

All data sets are protected from unauthorized or accidental access by individual, system, and file password protection.

The data are stored in three major data sets, namely (1) a raw data set, (2) a verified data set, and (3) a validated data set. These three data sets make up the ELS data base.

12.1 Raw Data Set

At Oak Ridge National Laboratory (ORNL), the field and analytical laboratory data (analytical results and data qualifiers - see Table 9.8) reported on Data Forms 1, 2, 11, 13, 18, 19, 20, 21, 22, and 23 are directly entered into the raw data base using the Statistical Analysis System (SAS). A copy of the data package consisting of these forms is also sent to the EPA EMSL-LV QA staff for concurrent data analysis. Data receipt is acknowledged, and field stations and the analytical laboratory verify that all forms are received by the data base management personnel.

The SAS full-screen editor procedure is used to provide gross error checking as data are entered. All data are entered into two separate data sets by two different operators. For the ELS-I data base, a custom program (COMPARE) has been developed in SAS to compare the two data sets and identify any inconsistencies. The advantage of this double entry and comparison process is that entry errors are removed from the system.

12.2 Verified Data Set

As the field and analytical laboratory data are transmitted and magnetic tapes of the raw data are made available to the EMSL-LV QA group, all data are evaluated and verified as described in Section 13.0. The data are processed by "Automated Quality Assurance Review, Interactive Users System" (AQUARIUS), an online QA system developed by the EMSL-LV QA staff. Reports generated by AQUARIUS range in subject from complex protolyte analysis to simple external/internal blank checks for QA purposes. AQUARIUS generates "exception tuples" that direct ORNL in flagging problem data, as deemed necessary by the EMSL-LV QA staff. Flags that are generated by AQUARIUS are given in Table 12.1. Exception tuples are defined as a grouped set of

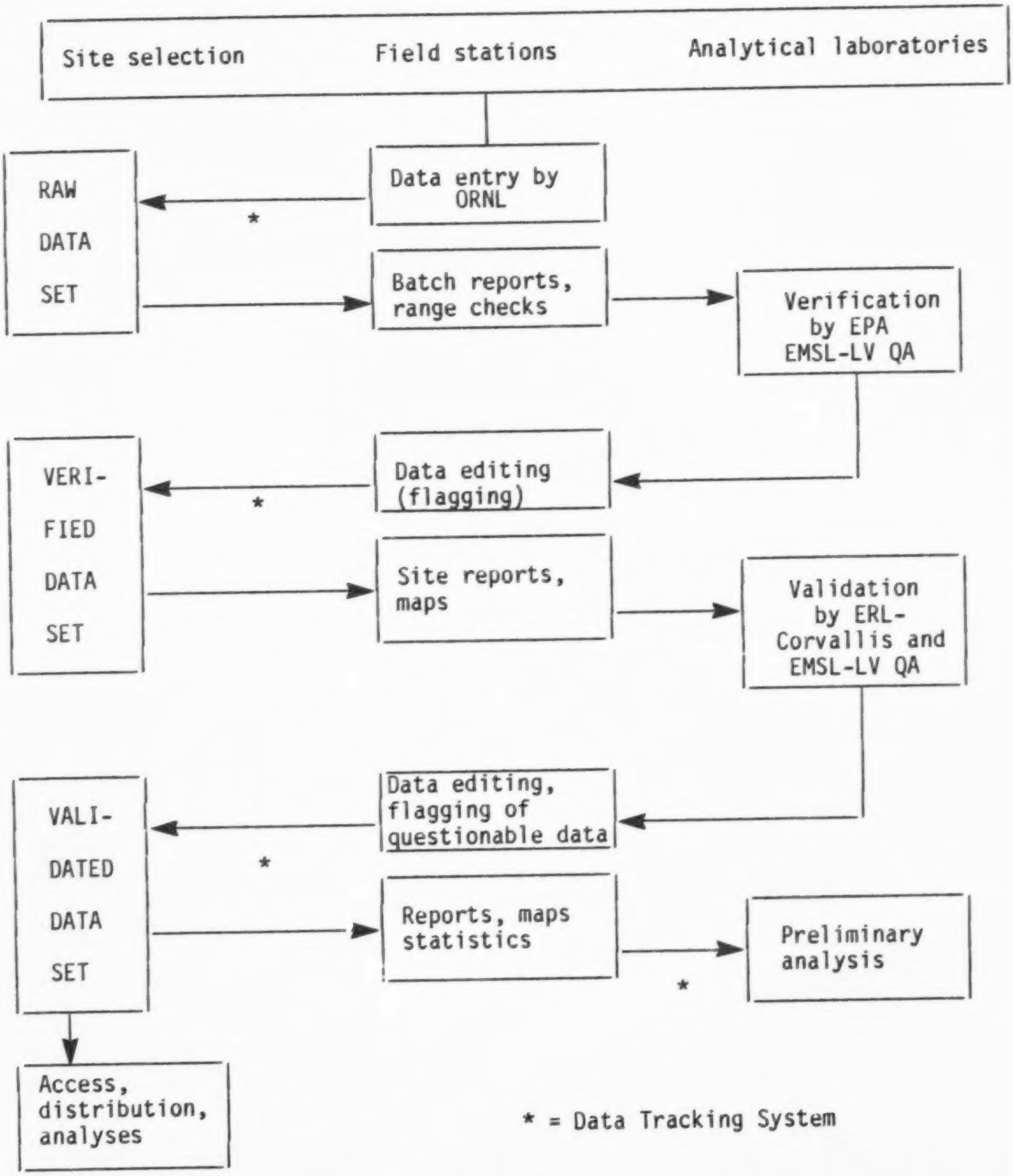

Site selection
Field stations
Analytical laboratories
Data entry by ORNL
RAW DATA SET
*
Batch reports, range checks
Verification by EPA EMSL-LV QA
Data editing (flagging)
VERIFIED DATA SET
*
Site reports, maps
Validation by ERL-Corvallis and EMSL-LV QA
Data editing, flagging of questionable data
VALIDATED DATA SET
*
Reports, maps statistics
Preliminary analysis
*
Access, distribution, analyses
* = Data Tracking System

Figure 12.1. Data management for the Eastern Lake Survey.

TABLE 12.1. DATA QUALIFIERS (FLAGS) FOR RAW DATA SET

A0	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to unknown cause.
A1	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to nitrate contamination.
A2	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to anion (other than nitrate) contamination.
A3	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to cation contamination.
A4	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to unmeasured organic protolytes (fits Oliver Model).
A5	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - anion concentration too high (list suspect anion).
A6	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - cation concentration too low (list suspect cation).
A7	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - anion concentration too low (list suspect anion).
A8	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - cation concentration too high (list suspect cation).
B0	External (field) blank is above expected criteria for pH, DIC, DOC, specific conductance, ANC, and BNC determinations.
B1	Internal (lab) blank is >2 x CRDL for pH, DIC, DOC, specific conductance, ANC, and BNC determinations.
B2	External (field) blank is above expected criteria and contributed >20% to sample values. (This flag is not used for pH, DIC, DOC, ANC, or BNC determinations.)

(continued)

TABLE 12.1. (Continued)

B3	Internal (lab) blank is >2 x CRDL and contributes >10% to the sample concentrations. (This flag is not used for pH, DIC, DOC, ANC, or BNC determinations.)
B4	Potential negative sample bias based on internal (lab) blank data.
B5	Potential negative sample bias based on external (field) blank data.
C0	% Conductance Difference (%CD) is outside criteria due to unknown cause (possible analytical error - ion concentration too high).
C1	% Conductance Difference (%CD) is outside criteria due to possible analytical error - anion concentration too high (list suspect anion).
C2	% Conductance Difference (%CD) is outside criteria due to anion contamination.
C3	% Conductance Difference (%CD) is outside criteria due to cation contamination.
C4	% Conductance Difference (%CD) is outside criteria due to unmeasured organic ions (fits Oliver Model).
C5	% Conductance Difference (%CD) is outside criteria due to possible analytical error in conductivity measurement.
C6	% Conductance Difference (%CD) is outside criteria due to possible analytical error - anion concentration too low (list suspect anion).
C7	% Conductance Difference (%CD) is outside criteria due to unmeasured protolyte ions (does not fit Oliver Model).
C8	% Conductance Difference (%CD) is outside criteria due to possible analytical error - cation concentration too low (list suspect cation).
C9	% Conductance Difference (%CD) is outside criteria due to possible analytical error - cation concentration too high (list suspect cation).
D0	External (field) duplicate precision exceeded the maximum expected % relative standard deviation (%RSD), but either the routine or the duplicate concentrations were <10 x CRDL.

(continued)

TABLE 12.1. (Continued)

D2	External (field) duplicate precision exceeded the maximum expected % relative standard deviation (%RSD), and both the routine and duplicate sample concentrations were ≥ 10 x CRDL.
D3	Internal (lab) duplicate precision exceeded the maximum contract-required % relative standard deviation (%RSD), and both the routine and duplicate sample concentrations were ≥ 10 x CRDL.
F0	% Conductance Difference (%CD) exceeded criteria when Hydrolab conductance value was substituted.
F1	Hillman/Kramer protolyte analysis program indicated field laboratory pH problem when Hydrolab pH value was substituted.
F2	Hillman/Kramer protolyte analysis program indicated unexplained field pH/DIC problem when Hydrolab pH value was substituted.
H0	The maximum holding time criteria were not met.
H1	No "Date Analyzed" data were submitted for reanalysis data.
L1	Instrumental Detection Limit (IDL) exceeded CRDL and sample concentration was <10 x IDL.
M0	Value obtained using a method which is unacceptable by the IFB contract.
N0	Audit sample value exceeded upper control limit.
N1	Audit sample value was below control limit.
N2	Audit sample value exceeded control limits due to suspect audit sample preparation.
N5	NO_3^- data obtained from analysis of aliquot 5.
P0	Field problem - station pH.

(continued)

TABLE 12.1. (Continued)

P1	Field problem - station DIC.
P2	Field problem - unexplained (pH/DIC).
P3	Lab problem - initial pH (ANC).
P4	Lab problem - initial pH (BNC).
P5	Lab problem - unexplained - initial pH (ANC or BNC).
P6	Lab problem - initial DIC.
P7	Lab problem - air-equilibrated pH/DIC.
P8	Lab problem - unexplained - initial pH/DIC.
P9	Lab problem - ANC determination.
Q1	QCCS was above contractual criteria.
Q2	QCCS was below contractual criteria.
Q3	Insufficient number of QCCS were measured.
Q4	No QCCS analysis was performed.
S0	Matrix spike % recovery (%REC) was above contractual criteria.
S1	Matrix spike % recovery (%REC) was below contractual criteria.
V	Data verified.

values that specify the batch, sample, and parameter to be flagged, modified, or verified. These exception tuples are then sent to ORNL via magnetic tape and are entered into the verified data set. The process might have to be repeated several times until all the data problems are resolved. The old data values are maintained in the raw data set as historical backup.

In addition to the standard QA analyses, AQUARIUS is used to generate various printouts supplied to the QA manager to point out intralab, interlab, and interfield bias, as well as discrepancies in blanks, audits, or other QA samples. The overall outcome is a verified data base in which all values either are qualified or replaced with missing value codes (listed in Table 12.2). The QA personnel coordinate with the field stations and the analytical laboratories to make all appropriate corrections in the data.

12.3 Validated Data Set

A computer printout of the verified data set is provided to the ERL Corvallis staff who initiate the validation process. The validation process increases the overall integrity of the data base by evaluating all data for internal and regional consistency using all the QA/QC information available.

The validation process compares data for a set of variables against a much narrower range utilizing knowledge of relationships in aquatic chemistry and limnology to identify intrasite sample inconsistencies. Intersite validation consists of comparing single site values with adjacent sites within a region. Data for groups of sites are compared and mapped to check for consistency. The validation process is discussed further in Section 14.0. After undergoing this reviewing process, the data, site by site, are transferred to the validated data base. The data will then be released by the EPA and will be made available to all data users.

TABLE 12.2. MISSING VALUE CODES

A - Carbonate alkalinity, CO_2-Acidity and mineral acidity data are eliminated from data base due to method inconsistencies.

C - Temporary flag indicating raw data incomplete pending confirmation by analytical laboratory.

N - Eliminate from data set pending review of aliquot 5 nitrate data.

R - Temporary flag indicating raw data incomplete pending reanalysis.

X - Permanent flag indicating invalid data based on QA review.

. - Value never reported.

(Note: These codes appear in numeric fields only.)

13.0 DATA EVALUATION AND VERIFICATION

As the field and analytical laboratory data are received by the EMSL-LV QA staff, all data are evaluated based on the available QA/QC information, using the established and organized review process described here. The objective of the data verification process is to identify and correct, flag, or eliminate data of unacceptable quality. Computer programs have been developed to automate this process as much as possible. Each batch of data is evaluated on a sample-by-sample basis, as described in the following subsections.

13.1 Field Data Review

Each field data form is reviewed to check for the following items:

1. Lake ID. Form 1 is compared to Form 2 to identify and correct transcription errors.
2. Trailer Duplicate. On Form 2 should be recorded a duplicate lake ID that matches a routine lake sample ID.
3. Hydrolab Calibration Data. The pH and specific conductance calibration data on Form 1 are compared to data on the Hydrolab calibration forms to ensure that initial calibration criteria are met; if the criteria are not met, correct data qualifiers are noted.
4. Hydrolab pH. The pH reading at 1.5 m, recorded on Form 1, is compared to the field laboratory pH reading on Form 2.
5. Field laboratory (trailer) pH and DIC. Form 2 measurements for field audit samples are evaluated in accordance with the associated acceptance criteria. Routine duplicate pairs and trailer duplicate pairs are evaluated for precision.
6. pH and DIC QCCS Data. Form 2 QCCS data are evaluated to ensure that QCCS criteria are met.

Data anomalies are reported to the field laboratory coordinator for review, and data reporting errors are reported to ORNL to be corrected before entry into the raw data set. All telephone communications are recorded in bound notebooks and data corrections are annotated on the appropriate forms.

13.2 Analytical Data Review

13.2.1 Daily QA Communications - Daily calls are made to each field station and analytical laboratory (1) to ensure that QA/QC guidelines are being followed, (2) to ensure that samples are being handled and analyzed properly, (3) to obtain current sample data, and (4) to discuss problems that may occur during analyses.

The primary objective of these calls is to identify and resolve issues quickly, before they affect data quality or interfere with the completion of the survey.

Preliminary sample data are obtained verbally, by computer, or by TELEFAX, depending on the analytical laboratory. The preliminary data are evaluated by comparing the QA sample data against acceptance criteria.

Responsible parties are notified of problems and all interactions are recorded in bound notebooks.

13.2.2 Preliminary Review of Sample Data Package - The sample data packages are reviewed for completeness, internal QC compliance, and appropriate use of data qualifiers. The Data Package Completeness Checklist (given in Appendix F) is used to assure consistency in the review of all data packages. Any discrepancies related to analytical data are reported to the appropriate analytical laboratory manager for corrective action. If discrepancies affect billing or data entry, then SMO or ORNL is notified. Comments provided in the cover letter are also reviewed to determine their impact on data quality and the need for any follow-up action by the laboratory. This data review process is also important in verifying that the contractual requirements are met for the purpose of payment.

13.2.3 Review of QA/QC Data - The analytical data reported on data forms are entered into the raw data set by ORNL as the data packages are received. A magnetic tape containing raw data is sent to the EPA IBM 3081 at the National Computer Center (NCC), Research Triangle Park, North Carolina. Each tape received by the NCC tape library is given a volume serial number and a BIN number that indicates the physical location of the tape. The tape is loaded remotely by the EMSL-LV QA staff, and exception programs, listed in Table 13.1, are generated.

The ELS-I Verification Report listed in Appendix G is completed with the use of outputs from exception reports (along with the original data and field notebooks). The verification report is a worksheet designed to systematically guide the auditor through the verification process by explaining how to flag data, tracking data resubmissions, tracking reanalysis and confirmation requests, listing the steps to help explain the QA exceptions, summarizing all modifications to the raw data base, and listing all verified sample data.

One hundred percent of the analytical data are verified, sample by sample. A routine lake sample has to meet both the anion/cation %ID

TABLE 13.1. EXCEPTION-GENERATING AND DATA REVIEW PROGRAMS

Program	Type
Exception-Generating Programs:	
1 = Audit Sample Summary	(LH,LL,FH,FL,FN)
2 = Lab/Field Blank Summary	(B,LB,FB)
3 = Field Duplicate Precision Summary	(R/D Pairs)
4 = Instrumental Detection Limit Summary	(All Species)
5 = Holding Time Summary	(All Species)
6 = % Conductance Difference Calculations	(All Species)
7 = Anion/Cation Balance Calculations	(All Species)
8 = Internal Lab Duplicates	
9 = Matrix Spike Summary	
10 = Protolyte Analysis (DIC, DOC, pH, ANC, and BNC Data Evaluation)	
11 = Reagent/Calibration Blanks and QCCS	
Data Review Programs:	
1 = Raw Data Listing - Format for QA Manager	
2 = Complete Raw Data Listing - Format for Audit Staff	
3 = Comparison of Form 1 and Form 2	(pH and DIC)
4 = Comparison of Form 2 and Form 11	(pH and DIC)
5 = QA/QC Flag Summary	
6 = Modified Gran Analysis Program	

and %CD criteria in order to be verified, unless the discrepancy can be explained by either the presence of organic species (as indicated by the protolyte analysis program) or an obvious correctable reporting error.

Additional flags are applied to a given parameter, even though the verification is on a "per sample" basis, when the batch QA sample data do not meet the acceptance criteria for QA samples such as field blanks, field duplicates, or audit samples. Each parameter is also flagged if internal QC checks such as matrix spike recovery, calibration and reagent blank analytical results, internal duplicate precision, instrumental detection limits, QCCS analytical results, and required holding times do not meet specifications. The final source of flags is the protolyte analysis program. A detailed description of the evaluation of DIC, DOC, pH, ANC, and BNC data by the protolyte analysis program is given in Section 13.2.4. In all cases, the flags that are generated by the computer programs are reviewed by the auditor for reasonableness and consistency before being entered into the data base.

13.2.4 Computer Evaluation of DIC, DOC, pH, ANC, and BNC Data - An evaluative computer program performs data checks and uses carbonate equilibria and DOC data to identify analytical error and the source of protolytes (acidic or basic species) in the sample. Thus, the DIC, DOC, pH, ANC, and BNC data are rigorously evaluated in light of known characteristics of carbonate equilibria. The overall process of data evaluation based on carbonate equilibria is summarized below.

13.2.4.1 Redundant Alkalinity Checks for pH and DIC - Evaluations of carbonate equilibria indicate that alkalinity is not affected by changes in dissolved CO_2 concentration. Furthermore, alkalinity can be calculated from carbonate equilibria if the DIC and pH are known. A theoretical alkalinity, C, is calculated from each of the three pH/DIC pairs:

C_1 = pH/DIC of "closed system" syringe samples (field laboratory)

C_2 = pH/DIC of "open system" samples (analytical laboratory)

C_3 = pH/DIC of "air-equilibrated system" samples (analytical laboratory)

The third data pair is obtained on an aliquot that has been equilibrated with standard air (300 ppm CO_2). If there is no analytical error, the three calculated alkalinities should agree within experimental error. The precision for calculated alkalinity values of less than or equal to 100 µeq/L should be within ±10 µeq/L and within ± 10 percent for calculated alkalinity values greater than 100 µeq/L. The precision windows are based on the estimated precision of the pH and DIC measurements used in the calculations. If this comparison indicates a potential analytical error (i.e., the precision limit is exceeded), the redundant pH and DIC values are compared to identify the source of error. Further evaluation of the QA/QC information for the individual data pairs usually identifies one of the pH or DIC measurements within the outlier pair as the source of error. Because of the redundancy in measurement, for every sample that is analyzed an acceptable pH or DIC value from one of the data pairs should be available to the data user.

13.2.4.2 Verification of Measured ANC - The measured ANC is evaluated by comparing it to the average of the acceptable calculated values for alkalinity determined during the evaluation of pH and DIC.

Carbonate Systems - For a true carbonate system, the measured ANC should equal (within experimental error) the calculated alkalinity. The difference between measured ANC and the calculated alkalinity should be within ±15 µeq/L for calculated alkalinities less than or equal to 100 µeq/L, and within ±10 percent for larger values. If the measured ANC differs from the calculated alkalinity, an analytical error is indicated in either the titration or in the pH or DIC measurements.

Mixed Systems - Mixed systems are those represented by samples that have significant concentrations of other protolytes in addition to the carbonate species. In natural waters, organic bases derived from humic and fulvic acids are often present and can have a significant contribution to the ANC. Two empirical relationships among DOC, pH, and organic protolytes have been proposed by Oliver et al. (1983). The first relates the total organic protolyte to DOC, and the second relates the mass action quotient (pKo) of the organics present to the sample pH.

DOC and pH are measured in each sample. The empirical relationships (defined by the Oliver model) and the measured pH and DOC values are used to estimate the contribution of organic protolytes to the measured ANC. The measured ANC should equal, within experimental error, the sum of the calculated alkalinity and the estimated organic protolyte contribution, assuming that significant concentrations of other non-organic protolytes are not present and there is no analytical error. The precision should be within ±15 µeq/L for calculated ANC less than or equal to 100 µeq/L and within ±10 percent for larger values.

13.2.4.3 Verification of Measured BNC - BNC, unlike ANC, is affected by changes in dissolved CO_2 concentration. Therefore, evaluation and verification of those data cannot utilize as much redundancy as that of ANC data. Only the initial pH and DIC values determined in the analytical laboratory (data pair C_2) can be used to calculate BNC for comparison with the measured value. As with ANC, other protolytes can contribute to the measured BNC. An estimate of CO_2-acidity is calculated from data pairs and carbonate equilibria. The calculated acidity should equal, within experimental error, the measured BNC, if no other protolytes are present. Precision for calculated acidity values less than or equal to 100 µeq/L should be within ±10 µeq/L and within 10 percent for larger values. If the calculated acidity is greater than the measured BNC, an analytical error in the pH, DIC, or BNC determination is indicated.

The pH and DIC measurements are verified by the previous tests (QA/QC redundancy and alkalinity checks). If the calculated acidity is less than the measured BNC, the difference may be due to the presence of other protolytes or to an analytical measurement error. The Oliver model is used to evaluate the contribution from organic acids.

13.2.4.4 System Check for Total Carbonate - For a carbonate system, it can be shown that the sum of alkalinity and acidity equals total carbonate concentration in the sample. For a mixed system, it can be shown that the sum of ANC and BNC equals the total protolyte concentration in the sample. Thus, the calculated values of alkalinity and acidity can be combined and compared to the sum of the measured ANC and BNC, as an additional check of the data. For a carbonate system, the sum of ANC and BNC should equal, within experimental error, the total carbonate concentration or the sum of calculated acidity and alkalinity. If this sum is less than the calculated total carbonate, an analytical error is indicated because the two titrations must account for all carbonate species present in the sample. Other protolytes or analytical error is indicated if the sum of ANC and BNC exceeds the calculated total carbonate. Again, the Oliver model is used to evaluate the data.

The precision for this evaluation should be within ±15 µmole/L for total carbonate concentrations less than or equal to 100 µmole/L, and ±10 percent for higher concentrations.

The protolyte analysis program generates flags (Table 12.1) based on the data checks described above to indicate the source of problems. Flowcharts demonstrating these data checks are available from EMSL-LV.

13.2.5 Follow-up with Analytical Laboratories - After the review of all data is completed, the analytical laboratories are requested to resubmit data reporting forms that are incomplete, submit corrections of previously reported data, confirm previous results, and reanalyze certain samples that do not meet QA/QC criteria. The analytical laboratories are directed to respond within a reasonable time so that the results are evaluated in time for them to be useful to the survey.

13.2.6 Preparation and Delivery of Verification Tapes - The steps identified in sections 13.2.2 through 13.2.5 are followed to identify suspect data and to correct erroneous data. The information obtained by this process is accumulated by the EMSL-LV QA staff and is placed on magnetic tapes, which are sent to ORNL. There, the new data are entered into the raw data set, to correct and flag the original data. These steps may have to be repeated several times before all the data are verified.

14.0 DATA VALIDATION

14.1 Overview

Validation, used in the context of data bases, is the process by which data are evaluated for quality consistent with the intended use of the information. Because validation is a process linked to the goals and methods of a project, the process must be defined for each data base. Consequently, no single set of criteria can be applied to all data bases to judge their validity. Validation is, therefore, a functional term for describing the continuing process of defining the quality of the data with each step resulting in increased knowledge of, and presumably confidence in, the data. This is accomplished by reviewing the data for errors; data known to be erroneous are identified so that correct data can be substituted, and possible errors are flagged to alert the user to their questionable status.

In the verification step, which precedes validation, the quality of the analytical chemical data is determined through a rigorous protocol based on known principles of chemistry. However, not all potential errors in the data are evaluated in the verification process. Therefore, the purpose of the validation process for the ELS-I is to investigate errors in the chemical analyses not detected in verification, and to provide a review of the quality of the nonchemical variables. The list of physical variables subject to validation is shown in Table 14.1.

Two aspects of the data validation process are the identification of outliers and the evaluation of possible systematic error in the measurement process. Both of these aspects are exploratory, as opposed to test-oriented, and as such, the methods stress visual presentations and subjective, though conservative, selection procedures. The objective is to attract attention to certain data values or sets of values in order that special thought and caution be given them when considering analysis or model-building based upon them. The methods selected for detection of outliers and systematic errors were chosen for their simplicity of implementation from a computational standpoint, using pre-existing software whenever possible. The process of validation is summarized in Figure 14.1.

14.2 Detection of Outliers

Outliers, observations that are not typical of the population from which the sample is drawn, are identified using univariate, bivariate, and multivariate analyses.

These procedures assist in identifying outliers that require further scrutiny. However, observations that are atypical with respect to the

TABLE 14.1. PHYSICAL VARIABLES SUBJECT TO VALIDATION

Variable	General Description of Validation Checks
1. Latitude	Lake location, as measured by LORAN, is maps.
3. Lake Elevation	Lake characteristics are checked against state records, where available, to confirm lake identification.
4. Lake Area	
5. Watershed Area	
6. Site Depth	
7. Stream Inlets and Outlets	
8. Lake Hydrologic Type	
9. Shoreline Land Use	Data are compared to aerial photographs.
10. Water Temperature	Recorded temperature is checked to see if it falls in appropriate range.
11. Secchi Disk Transparency	Data are checked for internal consistency.
12. True Color	
13. Turbidity	

population may result from analytical error or heterogeneity in chemistry among lakes. It is essential to separate analytical errors from abnormal lake chemistry to avoid the undesirable effect of purging analytically correct values from the data base (discussed Section 14.4).

14.2.1 Univariate Analyses - An initial approach to outlier detection is to consider each variable individually, searching for values that are extreme with respect to the sample. The method used here is the boxplot (Tukey, 1977) as implemented in MINITAB (Ryan et al., 1981) and SAS (SAS Institute, 1982). The boxplot summarizes the data for one variable based on the median and upper (Fu) and lower (Fl) fourths or quartiles. The difference between the upper and lower quartiles is known as the inter-quartile range (Fu - Fl = dF); any value greater than the absolute value of 3 dF is identified as an outlier.

14.2.2 Bivariate Analyses - Although values of two variables may not be be considered extreme relative to some expected or typical relationship. Scatter plots are useful for examining expected theoretical or empirical relationships between variables. The bivariate relationships examined

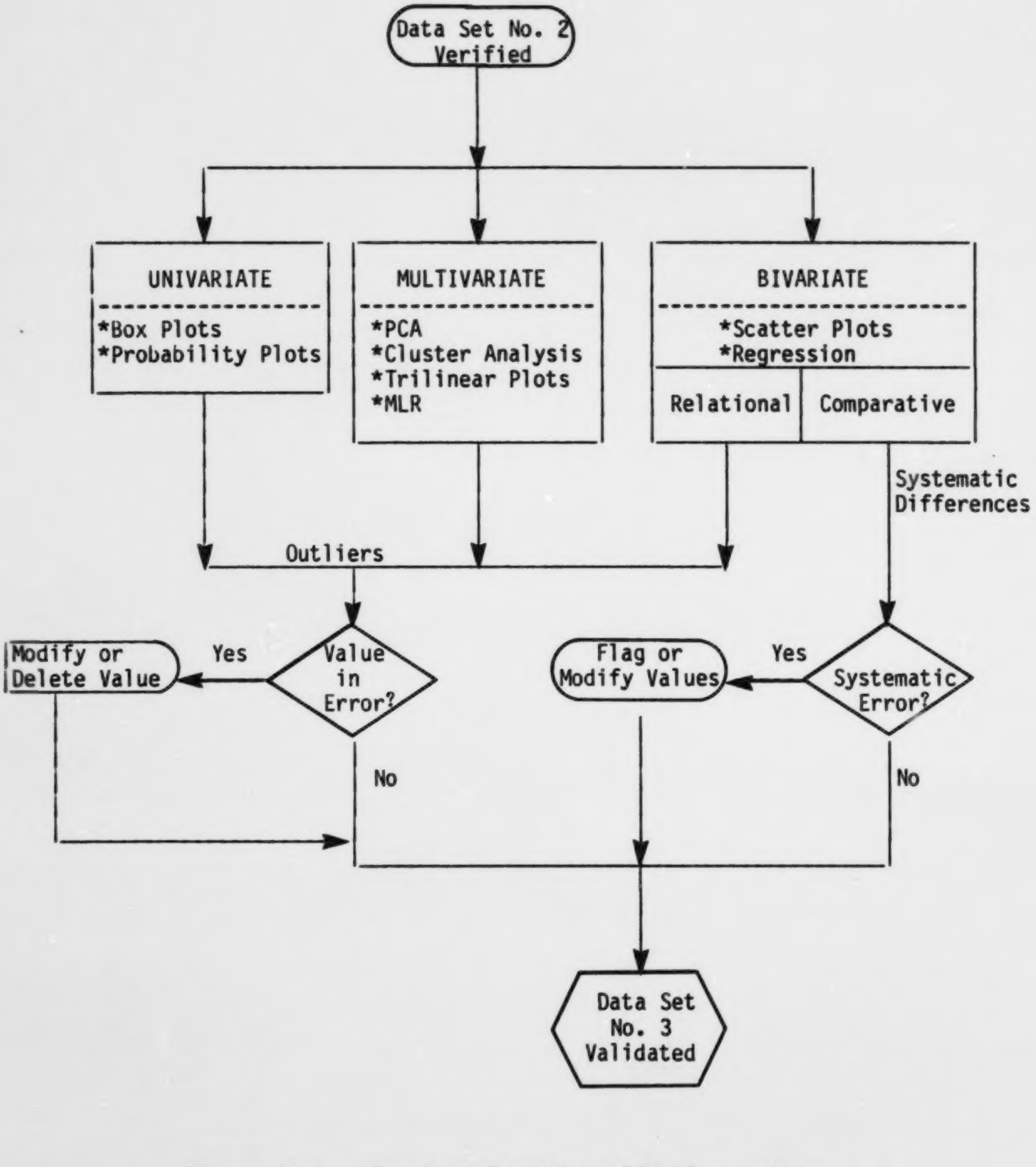

Data Set No. 2 Verified
UNIVARIATE
*Box Plots
*Probability Plots
MULTIVARIATE
*PCA
*Cluster Analysis
*Trilinear Plots
*MLR
BIVARIATE
*Scatter Plots
*Regression
Relational
Comparative
Systematic Differences
Outliers
Value in Error?
Yes
Modify or Delete Value
No
Systematic Error?
Yes
Flag or Modify Values
No
Data Set No. 3 Validated

Figure 14.1. Flowchart for data validation process.

in this process are shown in Table 14.2. Outliers are identified by visual inspection of the plots and by listing of residuals based on a least squares regression analysis where a linear relationship exists. Observations are identified as outliers if the absolute value of the standardized residual [(actual-predicted)/residual standard deviation] is generally greater than 3. Because the least squares analysis can be strongly biased by certain types of outliers, the residuals from resistant line fits, lines fit through the medians of partitions of the data (Velleman and Hoaglin, 1981), are examined for DOC, true color, turbidity, and Secchi disk transparency. Other variables are treated by use of an iterative process of linear regression, identification and removal of outliers, and repeated linear regression to identify additional outliers that would not have necessarily been identified had major outliers not been removed first.

14.2.3 Multivariate Analyses - Although examination of scatter plots is an important and necessary step for evaluating possible errors in the data, bivariate analyses must be limited to those variables that have obvious associations. The magnitude of the data set precludes examination of all possible distributions and bivariate plots. For example, the number of bivariate plots required for all combinations of the analytical variables exceeds 4,600. Although many of these combinations of variables are of no interest, many combinations remain. Clearly, this is not a practical or efficient method for examining all the data.

An alternative method of examining data for systematic and random errors is through multivariate analysis in which several variables are examined simultaneously. Because theoretical relationships are expected to exist among certain chemical variables, it is useful to examine these sets of variables as groups (Table 14.3).

Two primary multivariate techniques are used to identify outliers: cluster analysis and principal component analysis (PCA). Cluster analysis is a classification technique for identifying similarities (or, conversely, dissimilarities) among observations. Each observation is compared to other observations in the set and is assigned to a group or cluster using a measure of similarity.

The primary clustering technique used in the validation process is the FASTCLUS procedure in SAS (SAS Institute, 1982). This method is a non-hierarchical divisive method that is sensitive to outliers. A less formal clustering technique also used for selected samples is the Trilinear Diagram (Hem, 1970). The Trilinear Diagram is useful for examination of possible errors associated with the major cations and anions. The other clustering techniques are used for the related sets of variables shown in Table 14.3.

TABLE 14.2. PAIRS OF VARIABLES USED TO CHECK FOR RANDOM AND SYSTEMATIC ERRORS[a]

Specific Conductance (analytical laboratory)	vs.	Specific conductance (field)
		Calculated specific conductance
		Sum of cations
		Sum of anions
		Calcium
		Calcium and sodium
		pH (field laboratory)
		ANC
		DIC
ANC	vs.	Calcium
		pH (all measures)
		Sum of cations
		Sum of anions
		Calculated ANC (sum of base cations, $-SO_4^{2-}-Cl^-$)
pH (field laboratory)	vs.	pH (all measurements)
		Sum of cations
		Sum of anions
		Aluminum (total extractable)
		Sulfate (expressed as % of total anions)
DOC	vs.	True color
		Anion deficit
		Secchi disk transparency
		Turbidity
True Color	vs.	Anion deficit
		Secchi disk transparency
		Turbidity
Turbidity	vs.	Secchi disk transparency
Calcium	vs.	Magnesium
		Silica
Sodium	vs.	Chloride
DIC (equilibrated)	vs.	DIC (unequilibrated)
Aluminum (total)	vs.	Aluminum (total extractable)

---

[a] Bivariate plots and linear regressions are also prepared for variables analyzed on split samples using ICPAES (Inductively Coupled Plasma Atomic Emission Spectroscopy): Ca, Mg, Na, K, S, Si, P (total), Al (total), Fe, and Mn.

TABLE 14.3. RELATED GROUPS OF VARIABLES USED IN MULTIVARIATE ANALYSES

Group	Variables
1.	Major anions and cations
2.	pH, ANC, DOC, true color
3.	Turbidity, Secchi disk transparency, true color
4.	Nitrate, phosphorus, ammonium, turbidity, Secchi disk transparency
5.	Anion deficit, DOC, true color
6.	pH, total extractable aluminum, fluoride, DOC
7.	Silica, major cations
8.	Iron, manganese, total extractable aluminum, DOC
9.	ANC, DIC, pH
10.	pH, sulfate, DOC

Principal component analysis is a technique that also is commonly used to reduce large data matrices into manageable dimensions. New variables called principal components are formed from linear combinations of the original variables such that the first principal component reflects most of the variance or dispersion in the data. Each successive principal component explains less variance, and examination of the first several components is generally sufficient to describe the data. If the original data are approximately normally distributed, the resulting principal components are also approximately normal. Thus, a plot of any two components typically results in an elliptical cluster with outliers displaced from the ellipse.

Where appropriate, least squares multiple linear regression techniques also are used to identify observations with high absolute values of the standardized residual.

14.3 Detection of Systematic Error

Methods for evaluating systematic error are less exploratory because they require a source of external comparison. Here the tests are similar to comparison with standards (such as audits or split samples), with one major difference. The external references, consisting of data sets obtained from other investigators, cannot be viewed as "standards." Hence, a difference between data from the ELS-I and another data source does not necessarily imply that the ELS-I data are in error. However, comparisons with external data sources serve as aids for evaluating the quality of the data by bringing attention to data that may require additional scrutiny. Clearly, existence of systematic differences between the ELS-I data and several external data sources would be cause for careful reevaluation of the data in question.

Two types of systematic errors are investigated in the ELS-I data base: a constant additive effect (resulting in a nonzero intercept), or an effect that is dependent on the magnitude of the variable being measured (causing a slope $\neq 1$ or nonlinearity in the relationship). The "reference" data sets selected for systematic error are shown in Table 14.4. The external data sets used were selected based on the need to compare data from all three alkalinity classes, accessibility of the data, and documentation of QA procedures.

14.4 Treatment of Outliers and Systematic Differences

Data identified as outliers through the above procedures may be acceptable when evaluated in the context of other variables or when considering limitations of the methods used in the ELS-I. Therefore, before the original data sources are rechecked, the outliers and systematic differences identified in the validating process are reviewed for plausibility by the staff at ERL Corvallis. Data that remain suspect following screening by staff scientists are sent to the appropriate organization for reexamination.

Outliers and systematic differences for all chemical variables are checked against reported values by staff at EMSL-LV; site location and watershed-related variables are reviewed by the Geographic Research Team at ERL Corvallis; and remaining variables are checked by staff at ORNL. The data rechecking step for suspect values identified in validation of the chemical variables may reveal the following possible conditions and may require the associated response listed:

	Condition	Response
(1)	Suspect value in data set number 2 (verified data set) is found to be a transcription or transposition error.	Correct value is placed in data set number 3 (validated data set).

TABLE 14.4. EXTERNAL REFERENCE DATA SETS USED FOR IDENTIFYING SYSTEMATIC DIFFERENCES

Region/ Subregion	Political Boundary	Data Set	Number of lakes in common with NSWS	Variable Type	
				Physical	Chemical
1A	New York	-NY Dept. Environ. Conservation	17	X	
		-ADDNET	157	X	X
1C	Vermont	-Vermont Dept. of Environ. Control	58	X	
		-Long Term Monitoring	32	X	X
	New Hampshire	-N.H. Water Supply and Pollution Control Comm.	52	X	
1D	Massachusetts	-Dept. of Environ. Qual. Engr.	24	X	
1E	Maine	-Maine Dept. of Fish and Game	235	X	
		-Long Term Monitoring	6	X	X
2	Upper Midwest	-ADDNET	209	X	X
2A,B,C	Minnesota, Michigan, Wisconsin	-ERL-D/UMD	75	X	X
		-Long Term Monitoring	38	X	X
2C,D	Wisconsin	-Wisconsin County Surface Water Resources	287	X	
3A	Southern Blue Ridge Mountains	-ADDNET	48	X	
		-Long Term Monitoring	10	X	X
3B	Florida	-U.S.G.S. Hydrologic Almanac	36	X	
		-Aquatic Weed Survey	Not Resolved		X

(2)	Suspect value in data set number 2 agrees with reported value, and value was flagged in verification.	Value is flagged in data set number 3.
(3)	Suspect value in data set number 2 agrees with reported value, but value was not flagged in verification.	Value may be flagged in data set number 3 depending on evidence for possible error.

Values flagged in data set number 2, but not identified as aberrant in data validation, remain unchanged and flagged except in cases where the flag is not required for interpretation of the data; in these cases, the flag is removed. The protocol for resolution of outliers for the non-chemical variables is similar, with the exception that response (2) is omitted.

Resolution of systematic differences between the ELS-I and external reference data involves reexamination of the methods used to collect the ELS-I data. The effort involved in evaluating systematic differences depends on the evidence available to suggest that a bias may exist in the ELS-I data and the variable under consideration.

In most cases, sufficient information to perform an appropriate correction for bias in the ELS-I data is not likely to be available. However, the identification of a possible bias is provided to assist the user in interpreting such data.

15.0 REFERENCES

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1985. Standard Methods for the Examination of Water and Wastewater, 16th Ed. APHA, Washington, D.C.

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Costle, D. M., May 30, 1979(a). Administrator's Memorandum, EPA Quality Assurance Policy Statement. U.S. Environmental Protection Agency, Washington, D.C.

Costle, D. M., June 14, 1979(b). Administrator's Policy Statement, Quality Assurance Requirements for All EPA Extramural Projects Involving Environmental Measurements. U.S. Environmental Protection Agency, Washington, D.C.

Grubbs, F. E., 1969. Procedures for Detecting Outlying Observations in Samples. Technometrics, TCMTA, v. 11, n. 4, pp. 1-21.

Hem, J. D., 1970. Study and Interpretation of the Chemical Characteristics of Natural Water, 2nd Ed. U.S. Geological Survey Water Supply Paper 1473. U.S.G.S., Washington, D.C.

Hillman, D. C., J. F. Potter, and S. J. Simon, 1986. National Surface Water Survey Eastern Lake Survey (Phase I -- Synoptic Chemistry) Analytical Methods Manual U.S. Environmental Protection Agency, Las Vegas, Nevada.

Kramer, J. R., 1982. Alkalinity and Acidity. In: R. A. Minear and L. H. Keith (eds.), Water Analysis, Vol. 1. Inorganic Species, Part 1. Academic Press, Orlando, Florida.

McQuaker, N. R., P. D. Kluckner, and D. K. Sandberg, 1983. Chemical Analysis of Acid Precipitation: pH and Acidity Determinations. Environ. Sci. Technol., v. 17, n. 7, pp. 431-435.

Morris, F. A., D. V. Peck, M. B. Bonoff, and K. J. Cabble, 1986. National Surface Water Survey Eastern Lake Survey (Phase I --Synoptic Chemistry). Field Operations Report. U.S. Environmental Protection Agency, Las Vegas, Nevada.

Oak Ridge National Laboratory, 1984. National Surface Water Survey Project - Data Management Proposal. Environmental Sciences Division and Computer Sciences, UCC-ND, ORNL, Oak Ridge, Tennessee.

Oliver, B. G., E. M. Thurman, and R. K. Malcolm, 1983. The Contribution of Humic Substances to the Acidity of Colored Natural Waters. Geochim. Cosmochim. Acta, v. 47, pp. 2031-2035.

Omernik, J. M., and C. F. Powers, 1983. Total Alkalinity of Surface Waters -- a National Map. Annals of the Association of American Geographers, v. 73, pp. 133-136.

Omernik, J. M., A. J. Kinney, G. E. Griffith, and A. L. Yeaple. Total alkalinity of surface waters: a map of the Southeast and Southcentral region. Corvallis Environmental Research Lab, U.S. Environmental Protection Agency, Corvallis, Oregon (in preparation).

Omernik, J. M. and G. E. Griffith, 1985. Total Alkalinity of Surface Waters: a Map of the Upper Midwest Region. EPA-6001D-85-043, U.S. Environmental Protection Agency, Corvallis, Oregon.

Omernik, J. M. and A. J. Kinney, 1985. Total Alkalinity of Surface Waters: a Map of the New England and New York Region. EPA-6001D-84-216, U.S. Environmental Protection Agency, Corvallis, Oregon.

Peden, M. E., 1981. Sampling Analytical and Quality Assurance Protocols for the National Atmospheric Deposition Program. ASTM D-22 Symposium and Workshop on Sampling and Analysis of Rain, American Society for Testing and Materials, Philadelphia, Pennsylvania.

Ryan, T. A., B. L. Joiner, and B. F. Ryan, 1981. Minitab: Reference Manual. Pennsylvania State University, University Park, Pennsylvania.

SAS Institute, Inc., 1982. SAS User's Guide: Statistics. SAS, Cary, North Carolina.

Tukey, J. W., 1977. Exploratory Data Analysis. Addison-Wesley Publishing, Reading, Massachusetts.

U.S. Environmental Protection Agency, 1980. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans. QAMS-005/80. U.S. Environmental Protection Agency, Washington, D.C.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

U.S. Environmental Protection Agency, 1984a. National Surface Water Survey, Phase I. U.S. EPA, Office of Research and Development, Washington, D.C.

U.S. Environmental Protection Agency, 1984b. National Surface Water Survey, Phase I. Research Plan, A Summary of Contents. U.S. EPA, Corvallis, Oregon.

U.S. Environmental Protection Agency, 1984c. National Surface Water Survey, National Lake Survey - Phase I. NAPAP Project Reference No. E-23. U.S. EPA, Washington, D.C.

Velleman, P. F., and D. C. Hoaglin, 1981. Applications, Basics, and Computing of Exploratory Data Analysis. Duxbury Press, Boston, Massachusetts.

Weast, R. C. (ed.), 1972. CRC Handbook of Chemistry and Physics, 53rd Ed., CRC Press, Cleveland, Ohio.

APPENDIX A

DATA FORMS FOR REPORTING ANALYTICAL RESULTS

Page 1 of 2

NATIONAL SURFACE WATER SURVEY
FORM 11

SUMMARY OF SAMPLE RESULTS

LAB NAME ____________ BATCH ID ________ LAB MANAGER'S SIGNATURE ______________

SAMPLE ID:	ALIQUOT ID											
	1						2	3				
	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	Total Extr. Al mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	SiO_2 mg/L	ISE Total F^- mg/L
01												
02												
03												
04												
05												
06												
07												
08												
09												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												
21												
22												
23												
24												
25												
26												
27												
28												
29												
30												

NOTE: Approved data qualifiers and instructions for their use are listed in Table 9.7 of the QA Plan.

NATIONAL SURFACE WATER SURVEY
FORM 11

Page 2 of 2

SUMMARY OF SAMPLE RESULTS

LAB NAME ______________ BATCH ID ________ LAB MANAGER'S SIGNATURE ______________________

SAMPLE ID:	ALIQUOT ID											
	4		5								6	7
			Measured									
	DOC mg/L	NH_4^+ mg/L	Eq. pH	Alk Init. pH	Acy Init. pH	Acy µeq/L	Alk µeq/L	Spec. Cond. µS/cm	Eq. DIC mg/L	Init. DIC mg/L	Total P mg/L	Total Al mg/L
01												
02												
03												
04												
05												
06												
07												
08												
09												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												
21												
22												
23												
24												
25												
26												
27												
28												
29												
30												

Note: Approved data qualifiers and instructions for their use are listed in Table 9.8 of the QA plan.

Page 1 of 1

NATIONAL SURFACE WATER SURVEY
Form 13

ALKALINITY AND ACIDITY RESULTS

Lab Name____________ Batch ID____________ Sample ID____________
Lab Manager's Signature____________ Analyst____________

RESULTS

[Alk] = ____________ µeq/L
INITIAL SAMPLE VOLUME ____________ mL
BLANK ALKALINITY ____________ µeq/L

DATA

C_A = ____________ eq/L
DATE STANDARDIZED ____________
C_B = ____________ eq/L
DATE STANDARDIZED ____________

ACID TITRATION

VOLUME HCl (mL)	MEASURED pH'	CALCULATED pH
0.00		
0.00 (with KCl)		

BASE TITRATION

VOLUME NaOH (mL)	MEASURED pH'	CALCULATED pH
0.00		
0.00 (with KCl)		

NATIONAL SURFACE WATER SURVEY
Form 14*

Page 1 of 1

QC DATA FOR ALKALINITY
AND ACIDITY ANALYSES

LAB NAME ______________________ **BATCH ID** __________

LAB MANAGER'S SIGNATURE ______________________________

SAMPLE ID	Alk µeq/L	CO_2-Acy µeq/L	CALCULATED Alk		%X[b]
			RESULT	DIFFERENCE[a]	
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					
26					
27					
28					
29					
30					

*Form not required in data package but recommended for internal QC requirements.

[a] Difference = Calculated Alk-Measured Alk

$$^{b}\%X = \frac{\text{DIC (in µmoles/L)} - ([\text{Alk}] + [\text{CO}_2\text{-Acy}])}{\text{DIC}} \times 100$$

NATIONAL SURFACE WATER SURVEY
Form 15*

Page 1 of 1

SPECIFIC CONDUCTANCE

LAB NAME ____________ BATCH ID ____________ LAB MANAGER'S SIGNATURE ____________

Sample ID	SPECIFIC CONDUCTANCE (µS/cm)			CALCULATED SPECIFIC CONDUCTANCE FOR EACH ION µS/cm											
	Calculated	Measured	%CD**	HCO_3^-	Ca^{+2}	CO_3^{-2}	Cl^-	Mg^{+2}	NO_3^-	K^+	Na^+	SO_4^{-2}	NH_4^+	H^+	OH^-
01															
02															
03															
04															
05															
06															
07															
08															
09															
10															
11															
12															
13															
14															
15															
16															
17															
18															
19															
20															
21															
22															
23															
24															
25															
26															
27															
28															
29															
30															
Specific Conductance Factors of IONS [(µS/cm at 25°C) per mg/L]				0.715	2.60	2.82	2.14	3.82	1.15	1.84	2.13	1.54	4.13	3.5×10^5 (per mole/L)	1.92×10^5 (per mole/L)

*Form not required in data package but recommended for internal QC requirements.

$$**\%CD = \frac{\text{Calculated Specific Conductance - Measured Specific Conductance}}{\text{Measured Specific Conductance}} \times 100$$

Note: Reanalysis criteria are given in Table 9.5 of the QA plan.

NATIONAL SURFACE WATER SURVEY
Form 16*

Page 1 of 1

ANION-CATION BALANCE CALCULATION

LAB NAME ______________________ BATCH ID ________ LAB MANAGER'S SIGNATURE ______________

Sample ID	% Ion Difference **	Ions - (μeq/L)										
		Ca^{+2}	Cl^{-}	Mg^{+2}	NO_3^{-}	K^{+}	Na^{+}	SO_4^{-2}	F^{-}	NH_4^{+}	ALK	H^{+}***
01												
02												
03												
04												
05												
06												
07												
08												
09												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												
21												
22												
23												
24												
25												
26												
27												
28												
29												
30												
Factors to Convert mg/L to μeq/L		49.9	28.2	82.3	16.1	25.6	43.5	20.8	52.6	55.4	—	—

*Form not required in data package but recommended for internal QC requirements.

$$**\% \text{ Ion Difference } (\%ID) = \frac{ANC + \Sigma \text{ Anions} - \Sigma \text{ Cations (except } H^{+})}{\Sigma \text{ Anions} + \Sigma \text{ Cation} + ANC + 2[H^{+}]} \times 100$$

(Alk = ANC)

$$***[H^{+}] = (10^{-pH}) \times 10^{6}$$

NATIONAL SURFACE WATER SURVEY
Form 17

Page 1 of 1

IC RESOLUTION TEST

LAB NAME ______________________________

BATCH ID ______________________________

LAB MANAGER'S SIGNATURE ___________________________

IC Resolution Test

IC Make and Model: ____________________________

Date: __________________

Concentration: SO_4^{2-} ___________________ µg/mL, NO_3^- ____________ µg/mL

Column Back Pressure (at max. of stroke): ____________________ psi

Flow Rate: ________________ mL/min

Column Model: _______________________ Date of Purchase: ____________________

Column Manufacturer: _________________________________

Column Serial No: __________________________________

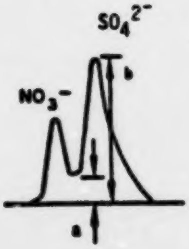
Is precolumn in system ___ Yes ___ No

(a) __________ cm (b) __________ cm

Percentage Resolution: 100 x (1-a/b) _________________________

The resolution must be greater than 60%

Test Chromatogram:



NATIONAL SURFACE WATER SURVEY
Form 18

Page 1 of 1

DETECTION LIMITS

LAB NAME ____________________ BATCH ID ____________________

LAB MANAGER'S SIGNATURE ____________________

Parameter	Units	Required Detection Limit	Instrumental Detection Limit*	Date Determined (DD MMM YY)
Ca	mg/L	0.01		
Mg	mg/L	0.01		
K	mg/L	0.01		
Na	mg/L	0.01		
Mn	mg/L	0.01		
Fe	mg/L	0.01		
Al, Total Extractable	mg/L	0.005		
Cl^-	mg/L	0.01		
SO_4^{2-}	mg/L	0.05		
NO_3^-	mg/L	0.005		
SiO_2	mg/L	0.05		
F^-, Total	mg/L	0.005		
NH_4^+	mg/L	0.01		
DOC	mg/L	0.1		
Specific Conductance	µS/cm	**		
DIC	mg/L	0.05		
P, Total	mg/L	0.002		
Al, Total	mg/L	0.005		

*To be calculated as required in Section 9.6 of the QA plan and filled out by the analytical lab

**Report the $\overline{X}$, which must not exceed 0.9 µS/cm, of six (6) nonconsecutive blanks

Note: Report with four significant figures or down to IDL

NATIONAL SURFACE WATER SURVEY
FORM 19

SAMPLE HOLDING TIME SUMMARY

LAB NAME ______________ BATCH ID ________ LAB MANAGER'S SIGNATURE ________________

DATE SAMPLED* ____________ DATE RECEIVED* _____

Parameter	Ca	Mg	K	Na	Mn	Fe	Total Extr. Al	Cl^-	SO_4^{2-}	NO_3^-	SiO_2	ISE Total F^-
Holding Time	28	28	28	28	28	28	7	28	28	7	28	28
Holding Time Plus Date Sampled												
Sample ID:				Date*				Analyzed**				
01												
02												
03												
04												
05												
06												
07												
08												
09												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												
21												
22												
23												
24												
25												
26												
27												
28												
29												
30												

*Report these dates as Julian dates (i.e. March 26, 1984 = 4086).
**If parameter was reanalyzed due to QA problems, report the last date analyzed.

NATIONAL SURFACE WATER SURVEY
FORM 19

Page 2 of 2

SAMPLE HOLDING TIME SUMMARY

LAB NAME ____________ BATCH ID ________ LAB MANAGER'S SIGNATURE ____________

DATE SAMPLED* ____________ DATE RECEIVED* ______

Parameter	DOC	NH_4^+	Eq. pH	Acidity	Alkalinity	Specific Conductance	Eq. DIC	Init. DIC	Total P	Total Al
Holding Time	14	28	7	14	14	14	14	14	28	28
Holding Time Plus Date Sampled										
Sample ID:			Date*			Analyzed**				
01										
02										
03										
04										
05										
06										
07										
08										
09										
10										
11										
12										
13										
14										
15										
16										
17										
18										
19										
20										
21										
22										
23										
24										
25										
26										
27										
28										
29										
30										

*Report these dates as Julian dates (i.e. March 26, 1984 = 4086).
**If parameter was reanalyzed due to QA problems, report the last date analyzed.

NATIONAL SURFACE WATER SURVEY
FORM 20

1 of 2

BLANKS AND QCCS

LAB NAME ____________ BATCH ID ________ LAB MANAGER'S SIGNATURE ____________

Parameter		ALIQUOT ID 1						2	3				
		Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	Total Extr.Al mg/L	Cl⁻ mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	SiO_2 mg/L	ISE Total F⁻ mg/L
Calibration Blank													
Reagent Blank		N	N	N	N	N	N	N	N	N	N		N
DL QCCS	Theoretical								N	N	N	N	N
	Measured								N	N	N	N	N
Low QCCS True Value													
Low QCCS Upper Control Limit													
Low QCCS Lower Control Limit													
Initial													
Continuing													
Continuing													
Continuing													
Continuing													
Continuing													
Final													
High QCCS True Value													
High QCCS Upper Control Unit													
High QCCS Lower Control Limit													
Initial													
Continuing													
Final													

Note: Approved Data Qualifiers and instruction for their use are listed in Table 9.8 of the QA plan.

116

NATIONAL SURFACE WATER SURVEY
FORM 20

2 of 2

BLANKS AND QCCS

LAB NAME ____________ BATCH ID ____________ LAB MANAGER'S SIGNATURE ____________

			ALIQUOT ID							
	4		5						6	7
			Measured							
Parameter	DOC mg/L	NH_4^+ mg/L	Eq pH	Alk pH	Acy pH	Spec. Cond. µS/cm	Eq. DIC mg/L	Init. DIC mg/L	Total P mg/L	Total Al mg/L
Calibration Blank			N	N	N					
Reagent Blank	N	N	N	N	N	N	N	N	N	
DL theoretical	N	N	N	N	N	N	N	N		
QCCS measured	N	N	N	N	N	N	N	N		
Low QCCS True Value										
Low QCCS Upper Control Limit										
Low QCCS Lower Control Limit										
Initial										
Continuing										
Continuing										
Continuing										
Continuing										
Continuing										
Final										
High QCCS True Value										
High QCCS Upper Control Limit										
High QCCS Lower Control Limit										
Initial										
Continuing										
Final										

Note: Approved Data Qualifiers and instruction for their use are listed in Table 9.8 of the QA plan.

NATIONAL SURFACE WATER SURVEY
FORM 21

Page 1 of 1

MATRIX SPIKES

LAB NAME______________ BATCH ID__________________ LAB MANAGER'S SIGNATURE____________________

	ALIQUOT ID														
	1						3					4		6	7
Parameter	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	SiO_2 mg/L	ISE Total F^- mg/L	DOC mg/L	NH_4^+ mg/L	Total P mg/L	Total Al mg/L
MS First (orig.) Sample ID															
Sample Result															
Spike Result															
Spike Added															
Percent Recovery															
MS Second Sample ID															
Sample Result															
Spike Result															
Spike Added															
Percent Recovery															
MS Third Sample ID															
Sample Result															
Spike Result															
Spike Added															
Percent Recovery															

Note: Matrix spikes not required for Aliquots 2 and 5.

NATIONAL SUFACE WATER SURVEY
Form 22

Page 1 of 2

DUPLICATES

LAB NAME ____________ BATCH ID ________ LAB MANAGER'S SIGNATURE ____________

	ALIQUOT ID											
	1						2	3				
Parameter	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	Total Extr.Al mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	SiO_2 mg/L	ISE Total F^- mg/L
Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD												
Second Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD												
Third Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD												

Note: Approved Data Qualifiers and instructions for their use are listed in Table 9.8 of the QA plan.

NATIONAL SURFACE WATER SURVEY
Form 22

Page 2 of 2

DUPLICATES

LAB NAME ___________ BATCH ID _________ LAB MANAGER'S SIGNATURE ____________________

	ALIQUOT ID											
	4		5								6	7
			Measured									
Parameter	DOC mg/L	NH_4^+ mg/L	Eq. pH	Alk Initial pH	Acy Initial pH	Acy μeq/L	Alk μeq/L	Spec. Cond. μS/cm	Eq. DIC mg/L	Init. DIC mg/L	Total P mg/L	Total Al mg/L
Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD*												
Second Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD*												
Third Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD*												

*Report the absolute difference instead of %RSD for pH determinations.

Note: Approved Data Qualifiers and instructions for their use are listed in Table 9.8 of the QA plan.

NATIONAL SURFACE WATER SURVEY
Form 23

Page 1 of 1

STANDARD ADDITIONS

LAB NAME ________ BATCH ID ______ SAMPLE ID _____ LAB MANAGER'S SIGNATURE ________

Parameter	ALIQUOT ID														
	1						3					4		6	7
	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	SiO_2 mg/L	ISE Total F^- mg/L	DOC mg/L	NH_4^+ mg/L	Total P mg/L	Total mg/L
MS First (orig.) Sample ID															
Single Response															
Spike added (Conc.)															
Sample Spike 1 Response															
Spike 2 Conc.															
Sample Spike 2 Response															
Calc. Sample Conc. for Orig. Sample (Summarized on Form 11)															

Note 1: Approved Data Qualifiers and instructions for their use are listed in Table 9.8 of the QA plan.
Note 2: Standard additions not required for Aliquots 2 and 5.

APPENDIX B

TELEPHONE RECORD LOG

TELEPHONE RECORD LOG

The daily communications with the analytical laboratory are entered into the Telephone Record Log or the laboratory notebook to track and resolve all problems encountered during analyses.

FACSIMILE

NATIONAL SURFACE WATER SURVEY PROGRAM
EMSL-LV-QA MANAGER/LABORATORY COMMUNICATION SYSTEM
QA/QC Telephone Record Log

Date of Call: ____________________

Laboratory Name: ____________________

Lab Contact: ____________________

EMSL-LV QA Contact or Designee: ____________________

Batch Number(s): ____________________

I. Initial and Continuing Calibration	Yes	No	If No: Recommended Corrective Action
A. Calibration blank is <CRDL			1. Check for baseline drift 2. Rezero if necessary
Comments:			
B. QCCS is analyzed immediately after calibration and is within control limits			
Comments:			1. Recalibrate instrument 2. Prepare working standards 3. Analyze a second QCCS 4. Invalidate results and repeat analysis
C. QCCS is analyzed every 10 samples and is within control limits			
Comments:			

FACSIMILE

I. (Continued)

	Yes	No	If No: Recommended Corrective Action
D. QCCS is plotted on a control chart (95 and 99% control limits are developed; acceptable range is ±10%) Comments:			
E. Calibration linearity is ≥0.99 Comments:			1. Check working standards 2. Make fresh standard 3. Repeat calibration
F. Instrument detection limits <CRDL Comments:			1. Invalidate results and 2. Repeat analysis
G. Reagent blank is ≤2 x CRDL Comments:			1. Eliminate source of contamination 2. Reanalyze samples that are associated with high blank

FACSIMILE

	Yes	No	If No: Recommended Corrective Action
II. Matrix Spike Analysis:			
A. Matrix spike recoveries are 85-115% Comments:			1. Spike 2 additional different samples. 2. If one or both are still out then analyze by standard additions
B. Samples are spiked at 2x the endogenous level or at 10 X IDL). Comments:			
III. Duplicate Sample Analysis or (RSD)			
A. RSD values are within the contract required control limits Comments:			1. Analyze a second different sample in duplicate 2. No further samples may be analyzed until duplicate sample results are within the control limits
B. RSD values are plotted on QC chart and 95% and 99% control limits are established Comments:			
IV. Ion Chromatography Resolution Test			
Resolution of the anion separator is $\geq$60% Comments:			1. Replace anion separator column 2. Repeat calibration

FACSIMILE

	Yes	No	If No: Recommended Corrective Action
V. Anion-Cation Balance Check			
Calculated percent Ion Difference (%ID) is less than the contract-recommended criteria.			Reanalyze samples Consult QA manager
Comments:			
VI. Conductance Balance Check			
Calculated percent conductance difference (%CD) meets the contract-recommended criteria.			Reanalyze samples Consult QA manager
Comments:			

Distribution: (1) Lab Copy, (2) EMSL-LV-QA Copy.

APPENDIX C

FIELD ON-SITE EVALUATION QUESTIONNAIRE

GENERAL (Page 1 of 1)

Questionnaire Completion Date ____________

Field Station ____

Location ____

Field Laboratory Supervisor ____________________________

Questionnaire Completed By (If more than one, indicate sections completed by each auditor.)

____

____

____

FIELD LABORATORY PERSONNEL (Page 1 of 1)

Position	Name	Academic Training*	Special Training*	Years Experience**
Field Laboratory Coordinator				
Field Laboratory Supervisor				
Analyst				
Analyst				
Analyst				

*List highest degree obtained and specialty. Also list years toward a degree.
**List only experience directly relevant to task to be performed.

FIELD LABORATORY - STANDARD OPERATING PROCEDURES (Page 1 of 1)

Item	Yes	No
Is the training manual followed in detail?		
Are copies available in the field station?		
Are analysis logbooks kept up to date?		
Are all on-site changes in procedures clearly documented and justified in field laboratory supervisor's logbook and approved by appropriate personnel?		

Comments:

FIELD LABORATORY FACILITIES (Page 1 of 1)

Item	Yes	No	Comment
Is the field station kept clean and organized?			
Are the refrigerator and freezer temperatures monitored on a daily basis and recorded in a logbook?			
Are waste disposal containers available and clearly labeled, and is waste disposed of properly?			
Are chemicals stored properly?			
Is balance calibration checked daily and recorded in a logbook?			
Is water supply purity monitored daily and recorded in a logbook?			

General Comments: ______________________________

FIELD LABORATORY EQUIPMENT (Page 1 of 6)

Color Test Kits

Item	Yes	No	Comment
Is manufacturer's operating manual readily available?			
Is kit cleaned and stored properly?			
Are viewing tubes kept clean?			
Is logbook kept up to date and signed daily?			
Is centrifuge maintained and kept clean?			

Comments:

FIELD LABORATORY EQUIPMENT (Page 2 of 6)

Nephelometer

Item	Yes	No	Comment
Is manufacturer's operating manual available?			
Is instrument kept clean?			
Are cuvettes kept clean and scratch-free?			
Is logbook kept up to date and signed daily?			
Is calibration checked before and after every 8 samples?			
Are standards kept refrigerated when not in use?			

Comments:

FIELD LABORATORY EQUIPMENT (Page 3 of 6)

Carbon Analyzer

Item	Yes	No	Comment
Is manufacturer's operating manual available?			
Is instrument kept clean?			
Is the injection valve flushed daily after use with deionized water?			
Is logbook kept up to date and signed daily?			
Is IR analyzer power left on at all times?			
Is standard stock solution prepared biweekly, and is QC stock solution prepared weekly; are they stored at 4°C?			
Are working standards prepared daily?			
Is exposure of samples and standards to the atmosphere minimized?			
Is required QC followed?			
Are pump tubes checked for wear and replaced on a regular basis (about every 2 weeks)?			
Are syringes and glassware cleaned properly after use?			
Are CO_2 and moisture scrubbers on standard bottles replaced when exhausted?			
Is tin scrubber in IR analyzer checked daily and refilled when necessary?			

Comments: ______________________________

____

FIELD LABORATORY EQUIPMENT (Page 4 of 6)

pH Apparatus

Item	Yes	No	Comment
Are meter and electrode operating manuals available?			
Is logbook kept up to date and signed daily?			
Is pH QC sample prepared daily?			
Is electrode stored in 3M KCl?			
Is required QC followed?			
Are electrodes checked and filled (if necessary) prior to use?			
Are sample chambers cleaned after use?			
Are buffers capped tightly after use?			

Comments: ____________________

FIELD LABORATORY EQUIPMENT (Page 5 of 6)

Filtration and Preservation Apparatus

Item	Yes	No	Comment
Is hood kept neat and clean?			
Is contamination evident?			
Is hood sealed when not in use?			
Is filtration apparatus kept ultraclean as specified?			
Are precautions taken to prevent contamination of filtrators, filter funnels, filters, sample bottles, and reagents?			
Is a water trap used with the vacuum pump?			
Are micropipets kept in an upright position at all times?			
Is the calibration of micropipets checked weekly?			
Are sample aliquots properly labeled?			
Is vacuum maintained at 10 to 12 inches Hg while filtering?			

Comments: ______________________________

FIELD LABORATORY EQUIPMENT (Page 6 of 6)

MIBK Extraction

Item	Yes	No	Comment
Is the centrifuge operating manual available?			
Is the extraction logbook kept up to date and signed daily?			
Is leakage of sample volume ($\geq$ 8.5 mL) noted in the logbook?			
Are reagents (NaOAc and hydroxyquinoline) made fresh daily?			
Is NH_4OH made fresh weekly and the preparation recorded in the logbook?			
Are pipets calibrated weekly?			
Is the 25 mL of standard measured accurately?			
Is the sample buffered to pH 8?			
Is the buffer/MIBK solution shaken vigorously for 10 seconds?			
Is disposal of solid and liquid wastes conducted properly?			

Comments: ______

SAMPLE PROCESSING (Page 1 of 1)

Item	Yes	No	Comment
Are all station documents kept in an orderly fashion?			
Are all forms completed as required and signed by supervisor?			
Is lab audit notebook kept up to date (labels inserted, etc.)?			
Are audit samples assigned different ID numbers from day to day?			
Are samples kept at 4°C when not being used?			
Are coolers containing sample kept in the shade and shut?			
Are freeze-gel packs kept frozen?			
Are samples properly packed for shipping (sealed, cooled to 4°C, individually wrapped, etc.)?			
Are 2 copies of the completed shipping form included with batch of samples?			

Comments: ______

FIELD SAMPLING CREW PERSONNEL (ELS-I) (Page 1 of 1)

Position	Name	Agency	Academic Training*	Special Training	Years Experience**
A. Field Duty Officer					
B. Team A					
1. Pilot					
2. Observer					
3. Sampler					
C. Team B					
1. Pilot					
2. Observer					
3. Sampler					
D. Team C					
1. Pilot					
2. Observer					
3. Sampler					
E. Team D					
1. Pilot					
2. Observer					
3. Sampler					

*List highest degree obtained and specialty. Also list years toward a degree.

**List only experience directly relevant to task to be performed.

FIELD SAMPLING (Page 1 of 1)

Item	Yes	No	Comment
Has adequate space been provided for predeparture activities?			
Are facilities clean and organized?			
Is equipment clean and organized?			

HYDROLAB CALIBRATION (Page 1 of 1)

Item	Yes	No	Comment
Are copies of the Hydrolab Manual available?			
Is the logbook kept up to date and signed daily?			
Is the instrument cleaned and stored properly?			
Is someone at the field station capable of performing the maintenance procedures described in the manual?			
Has any other maintenance been necessary?			
Are adequate spare parts (batteries, etc.) available?			
Are backup units available?			
Is the instrument performing well in the field?			
Are there any problems with the instrument?			
Is the person performing the calibration familiar with the procedures and control limits?			
Have there been any deviations from the standard procedures?			
Are the QC samples prepared each day?			
Is the instrument calibrated before and rechecked after each excursion?			

FIELD SAMPLING-PREPARATION (Page 1 of 1)

Item	Yes	No	Comment
Are checklists followed for loading equipment?			
Was sampling ever aborted due to forgotten items?			
Is equipment organized and easily accessible on sampling craft/vehicle?			
Is equipment stored properly to prevent injury or damage during transport?			
Are adequate plans for the excursion made and understood by personnel?			
Does the field base coordinator know where all teams are at any given time?			

FIELD SAMPLING-EN ROUTE (Page 1 of 1)

Item	Yes	No	Comment
Are the maps adequate?			
Are there problems locating lakes?			
Is camera operation understood?			
Are "lap cards" photographed at each lake?			
Are the Lake Data Forms understood and correctly filled out?			

FIELD SAMPLING-ON SITE (Page 1 of 1)

Item	Yes	No	Comment
Are there problems finding the deepest part of the lake?			
Is the depth recorder performing well?			
Are procedures clear and easily followed?			
Is required QC followed?			
Are required safety procedures followed?			
Are there any problems in determining stratification?			
Are Secchi disk guidelines being followed?			
Are adequate volumes of sample being taken?			
Are rinse procedures followed carefully?			
Are samples stored correctly?			
Are all forms filled out correctly?			
Is there effective coordination between the field sampling crews and the field laboratory personnel?			

APPENDIX D

ANALYTICAL LABORATORY ON-SITE EVALUATION QUESTIONNAIRE

GENERAL (Page 1 of 2)

Questionnaire Completion Date ________

Laboratory: ______________________________

____

Street Address: ______________________________

____

Mailing Address (if different from above): ______________________________

____

City: ______________________________

State: ______________________________ Zip: ________

Laboratory Telephone Number: Area Code: ______ No.: ____________

Laboratory Director: ______________________________

Quality Assurance Officer: ______________________________

Type of Evaluation: ______________________________

Contract Number: ______________________________

Contract Title: ______________________________

____

GENERAL (Page 2 of 2)

Personnel Contacted:

Name	Title

Laboratory Evaluation Team:

Name	Title

ORGANIZATION AND PERSONNEL (Page 1 of 3)

LABORATORY ORGANIZATIONAL CHART

ORGANIZATION AND PERSONNEL (Page 2 of 3)

Analytical Laboratory Personnel

Position	Name	Academic Training*	Special Training	Years Experience**

---

*List highest degree obtained and specialty. Also list years toward a degree.
**List only experience directly relevant to task to be performed.

ORGANIZATION AND PERSONNEL (Page 3 of 3)

Item	Yes	No	Comment
Do personnel assigned to this project have the appropriate educational background to successfully accomplish the objectives of the program?			
Do personnel assigned to this project have the appropriate level and type of experience to successfully accomplish the objectives of this program?			
Is the organization adequately staffed to meet project commitments in a timely manner?			
Does the QA officer report to senior management levels?			
Was the QA officer available during the evaluation?			

LABORATORY MANAGER (Page 1 of 1)

Item	Yes	No	Comment
Does the laboratory manager have his/her own copy of the standard operating procedures?			
Does the laboratory manager have his/her own copy of the instrument performance data?			
Does the laboratory manager have his/her own copy of the latest monthly QC plots?			
Is the laboratory manager aware of the most recent control limits?			
Does the laboratory manager review the following before reporting data: a. The data itself?			
b. The QC data sheet with analyst's notes?			
c. The anion/cation balance check?			
d. The calculated vs. measured sample specific conductance?			

STANDARD OPERATING PROCEDURES (SOP) (Page 1 of 1)

Item	Yes	No	Comment
Has SOP Manual been written?			
Is the SOP Manual followed in detail?			
Does it contain all QC steps practiced?			
Does each analyst have a copy at his/her disposal?			
Are plots of instrumental accuracy and precision available for every analysis?			
Are detection limit data tabulated for each analysis?			

LABORATORY FACILITIES (Page 1 of 4)

When touring the facilities, special attention should be given to: (a) the overall appearance of organization and neatness, (b) the proper maintenance of facilities and instrumentation, (c) the general adequacy of the facilites to accomplish the required work.

Item	Yes	No	Comment
Does the laboratory appear to have adequate workspace (12 sq. feet, 6 linear feet of unencumbered bench space per analyst)?			
Does the laboratory have a source of distilled/demineralized water?			
Is the specific conductance of distilled/demineralized water routinely checked and recorded?			
Is the analytical balance located away from draft and areas subject to rapid temperature changes?			
Has the balance been calibrated in the past year by a certified technician?			
Is the balance checked with a class S standard before each use and the check recorded in a logbook?			
Are exhaust hoods provided to allow efficient work with volatile materials?			
Is the laboratory maintained in a clean and organized manner?			

LABORATORY FACILITIES (Page 2 of 4)

Item	Yes	No	Comment
Are contamination-free work areas provided for the handling of toxic materials?			
Are adequate facilities provided for separate storage of samples, extracts, and standards, including cold storage?			
Is the temperature of the cold storage units recorded daily in logbooks?			
Are chemical waste disposal policies/ procedures adequate?			
Are contamination-free areas provided for trace level analytical work?			
Can the laboratory supervisor document that water free of trace contaminants is available for preparing standards and blanks?			
Do adequate procedures exist for disposal of waste liquids from the ICP and AA spectrometers?			
Is the laboratory secure?			
Are all chemicals dated on receipt and thrown away when shelf length is exceeded?			
Are all samples stored in the refrigerator between analyses?			

LABORATORY FACILITIES (Page 3 of 4)

Item	Available		Comments (where applicable, cite system, QC check, adequacy of space)
	Yes	No	
Filter room or desiccator (either is acceptable) maintained at 15° to 35°C and 50% relative humidity			
Gas			
Lighting			
Compressed air			
Vacuum system			
Electrical services			
Hot and cold water			
Laboratory sink			
Ventilation system			
Hood space			
Cabinet space			
Storage space (cite sq. ft.)			
Shared space			

LABORATORY FACILITIES (page 4 of 4)

COMMENTS ON LABORATORY FACILITIES

EQUIPMENT GENERAL (Page 1 of 1)

Item	Equipment			Condition/age			% of Time Used in Survey
	# of Units	Make	Model	Good	Fair	Poor	
Balance, analytical							
NBS-calibrated thermometer							
Desiccator							
Balance, top loader							
Class "S" weights							
Balance table							
Distilled water or deionized water - to meet Type I Reagent Grade specifications							
Glassware							
Drying oven							
Hot plates							

ICPES/AAS (Page 1 of 4)

Item	Manufacturer	Model	Installation Date
ICP			
Flame AAS			
Flame AAS			
Graphite Furnace AAS			
Data System			
Data System			

Comments on ICP/AAS Instrumentation:

ICPES/AAS (Page 2 of 4)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

ICPES/AAS (Page 3 of 4)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ____________			
Are all solutions properly labeled?			
Is the instrument properly vented?			
Is the interference correction automatically performed?			
Are dilute calibration standards prepared fresh weekly? Source ____________			

ICPES/AAS (Page 4 of 4)

Item	Yes	No	Comment
Is the QC check sample prepared from an independent stock? Source ______________			
Is the instrument allowed to warm up at least 15 minutes with the flame on before the final wavelength adjustment is made?			
Is the calibration curve at least a five-point curve?			
Is the first calibration curve of the day checked for detection limit and linearity?			
Are the matrix spike data calculated and plotted immediately after determination?			
Is each new calibration curve checked to see that the change in instrumental response is less than 5%?			
Are the following control samples analyzed with each run? Blanks			
QC Sample			
Spiked Sample			
Duplicates			
Does the analyst review the QC data sheet output by the data clerk, and then decide whether or not to release the data for reporting?			

ION CHROMATOGRAPH (Page 1 of 5)

Item	Manufacturer	Model	Installation Date
IC			
IC			
IC			
Autosampler			
Data System			
Precolumn			
Separator Column			
Supressor Column			

Comments:

ION CHROMATOGRAPH (Page 2 of 5)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

ION CHROMATOGRAPH (Page 3 of 5)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ____________			
Are all solutions properly labeled?			

ION CHROMATOGRAPH (Page 4 of 5)

Item	Yes	No	Comment
Are dilute calibration standards prepared fresh weekly? Source ______________			
If manual techniques are used, is eluant prepared fresh daily from the same concentrated stock buffer?			
Is the QC check sample prepared from an independent stock? Source ______________			
Is the calibration curve at least a four-point curve for each analytical range?			
Is the first calibration curve of the day checked for detection limit and recovery?			
Are the analyst spike data calculated and plotted immediately following determination?			
Are the following control samples analyzed with each run?			
Blanks			
QC Sample			
Spiked Sample			
Duplicates			
Does the analyst review the QC data sheet output by the data clerk, and then decide whether or not to release the data for reporting?			
Is the drip tray examined daily for reagent spills, and are spills cleaned up daily?			

ION CHROMATOGRAPH (Page 5 of 5)

Item	Yes	No	Comment
Are pumps oiled once per week?			
Is the anion precolumn cleaned as necessary?			
Is the SO_4^{2-}/NO_3^- resolution checked once per batch and documented?			

ACIDITY AND ALKALINITY (Page 1 of 4)

A. Manual System

Item	Manufacturer	Model	Installation Date
pH Meter			
Electrodes			
Data System			

Titration Apparatus (burets, etc.): ____________________

____

B. Automated System

Item	Manufacturer	Model	Installation Date
System			
Meter			
Electrodes			

Auto Titration Specifications: ____________________

____

____

Comments: ____________________

____

ACIDITY AND ALKALINITY (Page 2 of 4)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are entries in the notebook legible?			

ACIDITY AND ALKALINITY (Page 3 of 4)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printout, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ____________			
Are all solutions properly labeled?			
Are burets and/or micropipets calibrated weekly or more often?			
Is the stock 1.0 and 0.01 N NaOH standardized as required in methods manual?			
Are the correlation coefficients of the data examined to ensure that they are greater than 0.9990?			

ACIDITY AND ALKALINITY (Page 4 of 4)

Item	Yes	No	Comment
Does the analyst review the QC data sheet output by the data clerk, and then decide whether or not to release data for reporting?			
Are electrodes stored as recommended by the manufacturer?			
Are electrodes checked and filled, if necessary, before each analysis?			

pH (Page 1 of 4)

Item	Manufacturer	Model	Installation Date
Meter			
Electrodes			

Type of Temperature Compensation

Standard Gas Supplier

Standard Gas Specifications

Comments:

pH (Page 2 of 4)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

pH (Page 3 of 4)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ____________			
Are all solutions properly labeled?			
Is the pH meter calibrated before samples are analyzed?			
Is the pH meter calibration checked every batch as required in the methods manual?			
Is the pH electrode QC solution analyzed first and as specified, and are the results plotted immediately after determination?			

pH (Page 4 of 4)

Item	Yes	No	Comment
Does the material used as a QC sample meet specifications? Source of QCCS:			
Are the following control samples analyzed with each run: QCCS			
Duplicate			
Does the analyst review the QC data sheet output by the data clerk, and then decide whether or not to release data for reporting?			
Are electrodes stored as recommended by the manufacturer?			
Are electrodes checked and filled, if necessary, before each analysis?			

FLUORIDE ION SELECTIVE ELECTRODE (Page 1 of 3)

Item	Manufacturer	Model	Installation Date
Meter			
Electrodes			

Comments: ______

FLUORIDE ION SELECTIVE ELECTRODE (Page 2 of 3)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

FLUORIDE ION SELECTIVE ELECTRODE (Page 3 of 3)

Item	Yes	No	Comment
Are entries noting anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ____________			
Are all solutions properly labeled?			
Is there an electrode dedicated to low-level F^- analysis?			
Is all labware that comes in contact with standards and samples made of plastic?			
Is the temperature regulated?			
Is a multipoint calibration used?			

CARBON ANALYZER (Page 1 of 3)

Make and Model ______________________________

Specifications ______________________________

____

Comments: ___________________________________

____

____

____

____

____

____

____

____

CARBON ANALYZER (Page 2 of 3)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

CARBON ANALYZER (Page 3 of 3)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list __________			
Are all solutions properly labeled?			
Is CO_2-free water used to prepare standards?			
Are precautions taken to prevent CO_2 contamination of samples and standards?			
Is instrument designed to determine both DOC and DIC? If not, what modifications are necessary?			

AUTOMATED ANALYZER (Page 1 of 5)

Item	Manufacturer	Model	Installation Date
Automated Analyzer			
Electrodes			
Data System			

Comments:

AUTOMATED ANALYZER (Page 2 of 5)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his own copy of the instrument performance data?			
Does the analyst have his own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

AUTOMATED ANALYZER (Page 3 of 5)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ____________			
Are all solutions properly labeled?			
Are dilute calibration standards prepared fresh daily? Source ____________			
Is the QC check sample prepared fresh daily from an independent stock? Source ____________			

AUTOMATED ANALYZER (Page 4 of 5)

Item	Yes	No	Comment
Is the calibration curve at least a five-point curve?			
Is the first calibration curve of the day checked for detection limit(s) and linearity?			
Are the analyst QC sample data calculated and plotted real time?			
Is there an automated analyzer dedicated to each analysis (Total P, NH_4^+ SiO_2)?			
Is each new calibration curve checked to see that the change in instrumental response is less than 5%?			
Are the following control samples analyzed with each run?			
Reagent Blanks			
QCCS			
Spiked Sample			
Duplicates			
Does the analyst review the QC data sheet output by the data clerk, and then decide whether or not to release the data for reporting?			
Is water pumped through all lines daily, before and after analysis?			
Are pump tubes changed at least once every three days?			
Is the pump cleaned when the pump tubes are changed?			

AUTOMATED ANALYZER (Page 5 of 5)

Item	Yes	No	Comment
Is non-phosphorus-containing soap solution pumped through all lines once per week?			
Is the flowcell cleaned with a sulfuric acid-potassium dichromate solution once per month?			
Is the pump oiled once every three months? Date of last service _________			
Is the colorimeter mirror assembly and color filter cleaned and the alignment optimized once every three months? Date of last service _________			

SPECIFIC CONDUCTANCE (Page 1 of 3)

Item	Manufacturer	Model	Installation Date
Meter			
Conductivity Cell			

Is temperature compensated to 25°C? ____________________

What is the cell constant? ____________________

Comments: ____________________

SPECIFIC CONDUCTANCE (Page 2 of 3)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

SPECIFIC CONDUCTANCE (Page 3 of 3)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ____________			
Are all solutions properly labeled?			

DOCUMENTATION/TRACKING (Page 1 of 1)

Item	Yes	No	Comment
Is a sample custodian designated? If yes, what is the name of the sample custodian? Name ______________________			
Are the sample custodian's procedures and responsibilities documented? If yes, where are they documented?			
Are written Standard Operating Procedures (SOP's) developed for receipt of samples? If yes, where are the SOP's documented (laboratory manual, written instructions, etc.)?			
Are written Standard Operating Procedures (SOP's) developed for compiling and maintaining sample document files? If yes, where are the SOP's documented (laboratory manual, written instructions, etc.)?			
Are samples that require preservation stored in such a way as to maintain their preservation? If yes, how are the samples stored?			
After completion of the analysis, are the samples properly stored for 6 months or until laboratory personnel are told otherwise?			
Are the magnetic tapes stored in a secure area?			

ANALYTICAL METHODOLOGY (Page 1 of 2)

Item	Yes	No	Comment
Are the required methods used?			
Is there any unauthorized deviation from contract methodology?			
Are written analytical procedures provided to the analyst?			
Are reagent-grade or higher purity chemicals used to prepare standards?			
Are fresh working standards prepared daily?			
Are reference materials properly labeled with concentrations, date of preparations, and the identity of the person preparing the sample?			
Is a standard preparation and tracking logbook maintained?			
Do the analysts record bench data in a neat and accurate manner?			
Is the appropriate instrumentation used in accordance with the required protocol(s)?			

ANALYTICAL METHODOLOGY (Page 2 of 2)

COMMENTS ON ANALYTICAL METHODS AND PRACTICES

QUALITY CONTROL (Page 1 of 3)

Item	Yes	No	Comment
Does the laboratory maintain a QC Manual?			
Does the manual address the important elements of a QC program, including the following:			
a. Personnel?			
b. Facilities and equipment?			
c. Operation of instruments?			
d. Documentation of procedures?			
e. Procurement and inventory practices?			
f. Preventive maintenance?			
g. Reliability of data?			
h. Data validation?			
i. Feedback and corrective action?			
j. Instrument calibration?			
k. Recordkeeping?			
l. Internal audits?			

QUALITY CONTROL (Page 2 of 3)

Item	Yes	No	Comment
Are QC responsibilities and reporting relationships clearly defined?			
Have standard curves been adequately documented?			
Are laboratory standards traceable?			
Are QC charts maintained for each routine analysis?			
Do QC records show corrective action when analytical results fail to meet QC criteria?			
Do supervisory personnel review the data and QC results?			
Does the analyst have his/her own copy of the standard operating procedures?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest QC plots?			
Is the analyst aware of the most recent control limits?			
Does the analyst routinely review and report blank audit data to the laboratory manager?			

QUALITY CONTROL (Page 3 of 3)

Item	Yes	No	Comment
Does the analyst update control limits and obtain new control chart plots once per day of analysis?			
Are all QC data (control charts, regression charts, QC data bases, etc.) up to date and accessible?			
Are minimum detection limits calculated as specified?			
Is QC data sheet information reported to the analyst?			

DATA HANDLING (Page 1 of 2)

Item	Yes	No	Comment
Does data clerk do a 100% check for accuracy of data input to the computer?			
Are data calculations checked by another person?			
Are data calculations documented?			
Does strip chart reduction by on-line electronic digitizing receive at least 5% manual spot checking?			
Are manually interpreted strip chart data spot-checked after initial entry?			
Do laboratory records include the following information? Sample identification number			
Station identification			
Sample type			
Date sample received in laboratory			
Time, date, and volume of collection			
Date of analysis			
Analyst			
Result of analysis (including raw analytical data)			
Receptor of the analytical data			

DATA HANDLING (Page 2 of 2)

Item	Yes	No	Comment
Does laboratory follow required sample tracking procedures from sample receipt until discard?			
Does the data clerk routinely report QC data sheet information to the analyst?			
Does the data clerk submit QC data sheet information to the lab manager along with the analytical data to be reported?			
Do records indicate corrective action taken?			
Are provisions made for data storage for all raw data, calculations, QC data, and reports?			
Are all data and records retained the required amount of time?			
Are computer printouts and reports routinely spot-checked against laboratory records before data are released?			

SUMMARY (Page 1 of 2)

Item	Yes	No	Comment
Do responses to the evaluation indicate that project and supervisory personnel are aware of QA and its application to the project?			
Do project and supervisory personnel place positive emphasis on QA/QC?			
Have responses with respect to QA/QC aspects of the project been open and direct?			
Has a cooperative attitude been displayed by all project and supervisory personnel?			
Does the organization place the proper emphasis on QA?			
Have any QA/QC deficiencies been discussed before leaving?			
Is the overall QA adequate to accomplish the objectives of the project?			
Have corrective actions recommended during previous evaluations been implemented?			
Are any corrective actions required? If so, list the necessary actions below.			

SUMMARY (Page 2 of 2)

Summary Comments and Corrective Actions

199

APPENDIX E

EASTERN LAKE SURVEY

PREAWARD SCORING SHEET

200

EASTERN LAKE SURVEY
Preaward Audit Sample Scoring Sheet

Laboratory: ______________ Date: ______________

Quantitation: ______________ QA/QC ______________

Sample Set 1 ______________ Deliverables ______________

Sample Set 2 ______________

Total Score
(Maximum = 200 points)

PART I. QUANTITATION

	Points Awarded Sample Set 1 (Low Conc.)	Points Awarded Sample Set 2 (High Conc.)	Total Score
A. Aliquot 1 (Number of parameters within acceptance criteria x 12/6*)			
B. Aliquot 2 (Number of parameters within acceptance criteria x 8/1*)			
C. Aliquot 3 (Number of parameters within acceptance criteria x 14/5*)			
D. Aliquot 4 (Number of parameters within acceptance criteria x 8/2*)			
E. Aliquot 5 (Number of parameters within acceptance criteria x 30/5*)			
F. Aliquot 6 (Number of parameters within acceptance criteria x 4/1*)			
G. Aliquot 7 (Number of parameters within acceptance criteria x 4/1*)			

*Number of parameters present in aliquot. The scoring for pH and DIC will be based on the equilibrated values.

Laboratory: ______________________________ Date: ____________________

PART II. QUALITY ASSURANCE

	Possible Points	Points Awarded Sample Set 1	Points Awarded Sample Set 2	Total Score
A. Calibration/Reagent Blank Analyses:				
1. All results less than 2 x IDL.	2			
2. One result greater than 2 x IDL.	1			
3. Two results greater than 2 x IDL.	0			
B. Quality Control Check Sample				
1. All verifications within acceptance criteria.	5			
2. One or more verifications outside acceptance criteria.	0			
C. Matrix Spike Analyses:				
1. All percent recoveries within acceptance criteria or analyzed by method of standard additions.	2			
2. Percent recoveries outside acceptance criteria and not corrected by method of standard additions.	0			
D. Duplicate Sample Analyses:				
1. All RSD within acceptance criteria.	3			
2. 1-2 outside acceptance criteria.	2			
3. 3-4 outside acceptance criteria.	1			
4. 5 or more outside acceptance criteria.	0			

Laboratory: ______________________ Date: ____________

PART II. QUALITY ASSURANCE (Continued)

	Possible Points	Points Awarded Sample Set 1	Points Awarded Sample Set 2	Total Score
E. Anion-Cation Balance Calculation:				
1. Within acceptance criteria.	2			
2. Outside acceptance criteria.	0			
F. Detection Limits:				
1. All instrumental detection limits within acceptance criteria.	2			
2. One or more outside acceptance criteria.	0			

PART III. REPORTING AND DELIVERABLES

		Possible Points
A.	Data results submitted in acceptable format on standard forms.	2
B.	Quality assurance/quality control data supplied in acceptable format.	1
C.	Raw data supplied.	2
D.	Tabulated instrument detection limits and associated blank data supplied.	2
E.	Validation of results with signature of laboratory manager supplied.	1

APPENDIX F

EASTERN LAKE SURVEY

DATA PACKAGE COMPLETENESS CHECKLIST

EASTERN LAKE SURVEY

Data Package Completeness Checklist

Lab Name:____________________ Batch ID:____________________

Date: ____________________ Auditor's Initials:____________________

	Yes	Partial	No	Comments
1. All major difficulties during analyses have been discussed with the QA manager or designee.				
2. Anion/Cation balance and conductance balance checks exceeding criteria are reported on cover letter.				
3. a. Required forms (11, 13, 17, 18-23) submitted.				
b. Lab name, batch ID, and lab manager's signature submitted on all forms.				
c. Sample ID reported on Forms 13, 21, 22, and 23.				
d. Analyst's signature on Form 13.				
e. Correct units indicated on all forms.				
4. Form 11: a. Correct number of samples analyzed and results for each parameter tabulated.				
b. Data qualifiers (J, K, M, or U) reported when results are missing.				
c. Data qualifier R is reported when a sample is reanalyzed for QC purposes.				
d. F is reported as a data qualifier when a result is outside criteria (with consent of QA manager).				
e. G is reported as a data qualifier when the method of standard additions is used and Form 23 is submitted.				
f. Alk. Init. pH and Acy. Init. pH are within ±0.1 pH units.				
5. Percent IC resolution reported as greater than 60% on Form 17.				
6. Form 18: a. Instrumental detection limits and associated dates of determination tabulated.				
b. Instrumental detection limits less than or equal to the required detection limits (Table 4.1).				

(continued)

ELS (Continued)

	Yes	Partial	No	Comments
7. Form 19:				
a. Date sampled, date received, holding time plus date sampled, and dates of analyses for the correct number of samples are tabulated.				
b. Date analyzed is less than or equal to the reported holding time plus date sampled.				
c. The data qualifier H is reported for dates of analyses which exceed the holding time plus date sampled with consent of QA manager.				
8. Form 20: a. Calibration blanks, reagent blanks, and DL QCCS are reported where required.				
b. Calibration blanks and reagent blanks are less than 2 times the required DL.				
c. DL QCCS is approximately 2 times the required DL and the measured values are within 20% of the theoretical values.				
d. QCCS true values are in the midrange of sample values.				
e. If high QCCS true values are reported, the samples analyzed on high range are discussed in the cover letter.				
f. Diluted samples and their dilution factors are discussed in the cover letter.				
9. Percent recovery of matrix spikes is reported on Form 21 for each required analysis, and the values are within the range of 85 to 115%.				
10. Duplicate precision results are reported for each parameter and are less than or equal to the maximum %RSD (Table 4.1).				
11. Standard additions are performed and Form 23 is submitted when the matrix spike analyses do not meet contract requirements.				

Note: Checklist is not required in data package but is recommended to be included in the raw data.

APPENDIX G

EASTERN LAKE SURVEY
VERIFICATION REPORT

207

1.0 EASTERN LAKE SURVEY VERIFICATION REPORT

The NSWS Verification Report is used as a guideline to evaluate and verify National Surface Water Survey data.

The verification report is completed for every batch of data by deleting the inappropriate verb of a verb pair (i.e., are/are not, was/was not, etc.) and listing the affected samples and/or analyses. Those sections which do not apply are crossed out. Explanations of the reasons for flagging the data are necessary.

NSWS VERIFICATION REPORT

Batch No.	______	Field Station	______
Laboratory	______	Total No. of Samples	______
Date Audit Started	______	by	______
Date Audit Completed	______	by	______
Date Magnetic Tape to ORNL	______	Date Verification Final	______

1.1 Outstanding Issues: Contract Laboratory

1.1.1 Sample analysis (was, was not) complete based on data submitted. Reanalysis is recommended for the following samples:

Sample ID	Parameter	Reported Value	Date Requested	Date Submitted	Explanation

1.1.2 The Sample Data Package (was, was not) complete as submitted. The following data should be (re-)submitted:

Sample ID	Parameter	Date Requested	Date (Re-) Submitted	Explanation

208

1.1.2.1 The Sample Data Package (was, was not) complete as submitted. The following sample results should be confirmed by the contract laboratory:

Sample ID	Parameter	Date Requested	Date Confirmed	Explanation

1.2 Outstanding Issues: Sample Management Office (SMO)

1.2.1 Extenuating circumstances (were, were not) noted that would affect the assessment of holding time penalties. Penalties should be altered for the following samples:

Sample ID	Parameter	Old Penalty	Recommended Penalty	Explanation

1.2.2 Extenuating circumstances (were, were not) noted that would alter the sample data package delivery incentives or penalties. Incentives or penalties should be altered for the following samples (please put incentives in parentheses):

Sample ID	Old Penalty (or Incentive)	Recommended Penalty (or Incentive)	Explanation

1.2.3 Reanalysis (was, was not) required for this batch. The contract laboratory (should, should not) be paid for the following reanalysis:

Sample ID	Parameter	Explanation

Note: This section should be consistent with Sections 1.1.1. and 1.3.5.

1.2.4 Based on the review of the Sample Data Package and audit sample performance, the contract laboratory (should, should not) receive its entire 15% QA withholding. The contract laboratory should receive ___% of its maximum 15% QA withholding because the following internal QC checks exceeded contractual criteria:

1.3 Outstanding Issues: Oak Ridge National Laboratories (ORNL)

Summarize all modifications to the raw and verified data bases in the following sections:

Note: Only one transaction must be listed at a time because the field ID must be unique per transaction. Also, all of the following listings must be consistent with Sections 1.4 through 1.6

1.3.1 Attach the exception tuples summary which lists all the flags generated by the exception-generating and data review programs.

1.3.2 List any proposed modifications to the original raw data base, including sample values and tags. See Table 9.8 in Section 9.0 of this QA project plan for a listing of NSWS tags.

Sample ID	Field ID	Old Flag	New Flag	Old Value	New Value

1.3.3 List any modifications to the flags generated by the protolyte analysis and the exception-reporting programs (Table 13.1).

Sample ID	Field ID	Old Flag	New Flag	Old Value	New Value

1.3.4 List all samples that are flagged "V" to be transferred by the ORNL into the verified data base.

Sample ID	Field ID	Old Flag	New Flag	Old Value	New Value

1.3.5 List all missing value codes (given in Table 12.2) which replace questionable Form 11 sample values in the verified data base. Note that the missing value Code A replaces sample values for CO_3- Alkalinity, CO_2-Acidity, and Mineral-Acidity, and N replaces sample values for NO_3^-. These changes are made automatically by ORNL and need not be listed here.

Sample ID	Field ID	Old Flag	New Flag	Old Value	New Value

1.3.6 Attach the most current computer-generated summary of exception tuples. This list is the output of a manual edit of all the changes listed in Sections 1.3.1 through 1.3.5. The exception tuples list is updated to replace temporary missing value codes with Form 11 sample values (see Table 12.2 in this QA project plan). These changes are made to the raw data base and are copied via magnetic tape to the verified data base. This allows the verified and raw data bases to be updated simultaneously as Form 11 sample values are received from reanalysis or confirmation.

1.4 Anion/Cation Balance Check

NOTE: All flags generated in the following sections must be consistent with the computer-generated flag summary in Section 1.3.1.

1.4.1 Based on the Anion/Cation Balance Check Program, all samples submitted for this batch (were, were not) within criteria. The following samples are listed as exceptions:

Sample ID	Reported % Ion Bal. Diff. (%IBD)	Required % Ion Bal. Diff. (%IBD)	Explanation

1.4.1.1 Contamination (was, was not) indicated in the field and analytical lab blanks for the above exceptions. Contamination was apparent in the following samples:

Sample ID	Parameter	Explanation

The sample(s) listed above should be flagged "% Ion Balance Difference (%IBD) outside criteria due to anion, nitrate, or cation (circle one) contamination," using the appropriate sample flags "A1," "A2," or "A3."

1.4.1.2 Individual concentration values (were, were not) within the 95% confidence intervals for the subregion. The % Ion Balance Difference (%IBD) is recalculated using the expected value with the following results:

Sample ID	Parameter	Recalculated %IBD	Required %IBD	Explanation

For the samples listed above, the individual values outside the expected range should be confirmed or the samples should be reanalyzed by the analytical laboratory.

1.4.1.3 Unmeasured organic protolytes (were, were not) indicated by the protolyte analysis program for the exceptions listed in 1.4.1. The following samples appear to have %IBD outside criteria due to unmeasured organic protolytes:

Sample ID	Reported DOC (mg/L)	Nontitrated organic anions	Recalculated %IBD (Organic anions included)	Explanation

The samples listed above should be flagged "% Ion Balance Difference (%IBD) outside criteria due to unmeasured organic protolytes (fits Oliver model)," using the sample flag "A4."

1.5 Conductance Balance Check

1.5.1 Based on the Specific Conductance Check Program, all samples submitted for this batch (were, were not) within criteria. The following samples were listed as exceptions:

Sample ID	Reported % Cond. Dif. (%CD)	Max Required (%CD)	Explanation

1.5.1.1 The measured specific conductance (agrees, disagrees) with the field specific conductance for the exceptions listed above. The following samples had a laboratory conductance (greater, less) than the field conductance:

Sample ID	Measured Lab Conductance	Field (Hydrolab) Conductance	Explanation

1.5.1.2 The % Conductance Difference (%CD) is recalculated using the field specific conductance with the following results:

Sample ID	Old %CD	New %CD	Max Required %CD	Explanation

All samples which have the "new" %CD within criteria should be flagged "possible analytical error in conductance measurement," using the sample flag "C5." The laboratory should be required to reanalyze these samples. Summarize these values in Section 1.1.1.

1.5.1.3 Contamination (was, was not) indicated for the above exceptions. Contamination was apparent in the following samples:

Sample ID	Field Blank Contaminants	Explanation

The sample(s) listed above should be flagged "%CD outside of criteria due to suspected nitrate, anion, or cation contamination" (circle one) using the appropriate sample flag "C1," "C2," or "C3." If a misreported value is suspected, summarize it in Section 1.1.2.

1.5.1.4 Predicted values (were, were not) calculated for [ION] based on the concentration of the ions for the subregion. The %CD is recalculated using the predicted value with the following results:

Sample ID	Old %CD	New %CD	Max Required %CD	Explanation

The samples listed above that have the New %CD less than or equal to the Max %CD and the parameter(s) in question should be flagged "%CD out due to possible laboratory error in measurement of [ION]," using the appropriate sample flag "C1," "C6," "C8," or "C9."

1.5.1.5 Based on review of the protolyte analysis program, unmeasured organic ions (were, were not) suspected in the samples. The following samples are suspected to contain unmeasured organic ions:

Sample ID	Reported DOC (mg/L)	Explanation

All samples listed above should be flagged "%CD out due to unmeasured organic ions (Oliver model)," using the sample flag "C4."

1.5.1.6 Based on further review of protolyte analysis program data, other unmeasured protolyte ions (were, were not) suspected in the samples. The following routine samples are suspected to contain unmeasured protolyte ions:

Sample ID	Explanation

The samples listed above should be flagged "%CD out due to unmeasured protolyte ions (does not fit Oliver Model)" using the sample flag "C7."

1.6 Internal and External QC Data Review

1.6.1 All internal QC data (calibration blanks, reagent blanks, QCCS, lab duplicate precision, and matrix spike analyses) and external QC data (audits, field blanks, and field duplicates) are within expected criteria for all of the samples and the associated parameters except for:

Parameters: ______________________________

____

Sample ID's: ______________________________

____

1.6.2 All data for the following parameters and samples are not acceptable based on the following:

1.6.2.1 The external (field) blank (was, was not) within expected criteria. The parameters whose measurements were affected by contamination follow:

Parameter	Reported Value	Expected Range	Explanation

1.6.2.1.1 The external (field) blank (did, did not) contribute more than 20% to the other samples in the batch.

Sample ID	Parameter	% Contribution	Ref.	Explanation

All samples and parameters listed above should be flagged "Field blank contributes >20% to sample values" using the sample flag "B2."

1.6.2.2 The internal (lab) blank (was, was not) greater than 2 times the CRDL. The parameters whose measurements were affected by contamination follow:

Parameter	Reported Value	Required Criteria (2 x CRDL)	Explanation

Summarize the above in Section 1.2.4.

1.6.2.2.1 The internal (lab) blank (did, did not) contribute more than 10% to the other sample concentrations. The contaminated samples follow:

Sample ID	Parameter	% Contribution	Explanation

All samples and parameters listed above should be flagged "Internal blank is > 2 x CRDL and contributes >10% to the sample concentrations," using the sample flag "B3."

Summarize the above in Section 1.2.4.

1.6.2.3 For a routine/field duplicate sample pair with both concentrations greater than 10 times the CRDL, the field duplicate precision (was, was not) within expected criteria. The maximum expected %RSD is exceeded for the following analyses:

Parameter	Reported Value %RSD	Required %RSD	Explanation

The parameters listed above should be flagged "External (field) duplicates exceeded maximum %RSD, and both routine and duplicate sample concentrations are ≥ 10 x CRDL," using the sample flag "D2."

1.6.2.4 The internal (lab) duplicate precision (was, was not) met. Two additional duplicates (were, were not) run as required by the contract. The maximum expected %RSD was exceeded for the following analyses.

Parameter	Reported Value %RSD	Required %RSD	Explanation

The parameters listed above should be flagged "Internal (lab) duplicate precision exceeded required %RSD (Table 4.1) and both routine and duplicate sample concentrations are ≥ 10 x CRDL," using the parameter flag "D3."

Summarize the above in Section 1.2.4.

1.6.2.5 Audit sample data (were, were not) within the expected performance-based range. The following audit samples are outside the expected range:

Parameter	Audit Sample Type	Reported Value	Expected Range	Explanation

All samples in the batches associated with the audit sample analyses listed above should be flagged "Audit sample value exceeded control limits" using the appropriate parameter flag "NO," or "N1."

Summarize the above in Section 1.2.4.

1.6.2.6 The matrix spike % recovery (%REC) (was, was not) within contractual criteria. Standard additions (were, were not) performed as required by the contract. The following %REC's were outside the expected ranges:

Parameter	Reported %REC	Expected %REC	Explanation

All samples in the batches associated with the matrix spike analyses listed above should be flagged "Matrix spike % Recovery was outside 100 ± 15%" using the appropriate parameter flag "SO" or "S1."

Summarize the above in Section 1.2.4.

1.6.2.7 Internal Quality Control Check Sample (QCCS) data (were, were not) within control limits (Table 9.2) and the number of runs (were, were not) complete.

Parameter	Reported Value	Required Range	No. of QCCS Runs	No. of QCCS Runs Required	Explanation

All samples in the batches associated with the QCCS analyses listed above should be flagged "QCCS is outside contractual criteria," using the appropriate parameter flags "Q1" or "Q2" or, if appropriate "Q3" or "Q4."

Summarize the above in Section 1.2.4.

1.6.2.8 Samples (were, were not) analyzed on time. The maximum holding time criteria (Table 9.1) are exceeded for the following samples and the associated parameters:

Sample ID	Parameter	No. of Days Exceeding Holding Time Criteria	Explanation

All samples listed above should be flagged "The maximum holding time criteria were not met," using the sample flag "HO."

1.6.2.9 Instrumental detection limit (did, did not) exceed the required DL (Table 4.1). The following sample values reported at less than 10 times the IDL are in question:

Sample ID	Parameter	Reported Conc.	Reported IDL	Required DL	Explanation

All samples with concentrations <10 x IDL for the parameters listed above are in question and should be flagged "IDL exceeded CRDL," using the sample flag "L1."

If reanalysis is required, summarize the above in Section 1.1.